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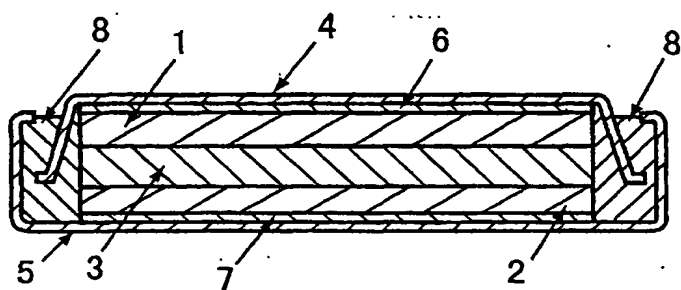
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**TER MEER STEINMEISTER & PARTNER GbR****Patentanwälte,****Mauerkircherstrasse 45****81679 München (DE)****(54) ELECTRODE FOR LITHIUM CELL AND LITHIUM SECONDARY CELL**

(57) In an electrode for a lithium battery having a lithium storing and releasing active thin film provided on a current collector, such as a microcrystalline or amorphous silicon thin film, the electrode is characterized in that the thin film is divided into columns by gaps formed

therein in a manner to extend in its thickness direction and that the columnar portions are at their bottoms adhered to the current collector.

FIG. 1



**Description****TECHNICAL FIELD**

5 [0001] The present invention relates to a novel electrode for use in lithium battery, a lithium battery and a rechargeable lithium battery utilizing the electrode.

**BACKGROUND ART**

10 [0002] The battery performance of rechargeable lithium batteries recently under intensive research and development, such as charge-discharge voltage, cycle life characteristics or storage characteristics, depends largely upon the types of the electrodes used. This has led to the attempts to better battery performance by improving electrode active materials.

15 [0003] The use of metallic lithium for the negative active material, although possible to construct a battery with high energy density per weight and volume, presents a problem that the lithium deposited on charge grows into dendrite which could cause internal short-circuiting.

[0004] Rechargeable lithium batteries are reported (Solid State Ionics, 113-115, p57 (1998)) which use an electrode consisting of aluminum, silicon, tin or the like that is electrochemically alloyed with lithium on charge. Among these, a silicon electrode provides a particularly high theoretical capacity and is promising as a high-capacity negative electrode. For this reason, various rechargeable batteries using silicon for the negative electrode are proposed (Japanese Patent Laying-Open No. Hei 10-255768). However, such alloying negative electrodes fail to provide sufficient cycle characteristics since alloys, as electrode active materials, are themselves pulverized on charge and discharge to reduce current-collecting capabilities.

**DISCLOSURE OF THE INVENTION**

[0005] It is an object of the present invention to provide a novel electrode which, when used as an electrode of a rechargeable lithium battery, can provide a high charge-discharge capacity and excellent charge-discharge cycle characteristics, and also provide a lithium battery and a rechargeable lithium battery utilizing the novel electrode.

30 [0006] The present invention is an electrode, for use in lithium batteries, characterized as comprising a thin film provided on a current collector, wherein the thin film contains active material capable of lithium storage and release and is divided into columns by gaps formed therein and extending in its thickness direction, and the columnar portions are at their bottoms adhered to the current collector.

35 [0007] In the present invention, the thin film composed of the active material is divided into columns by the gaps formed therein and extending in its thickness direction, so that spaces are provided in such a fashion as to surround the columnar portions. These spaces serve to relax a stress caused by expansion and shrinkage of the thin film on charge and discharge and thereby prevent the stress from increasing to the extent that causes falling-off of the thin film from the current collector. Accordingly, the columnar portions can be kept adherent at their bottoms to the current collector.

40 [0008] In the present invention, at least a half of thickness portion of the thin film is preferably divided into columns by the gaps. That is, a thickness portion of the thin film that occupies at least a half of its thickness is preferably divided into columns by the gaps.

45 [0009] Also, in the case where irregularities are formed on a surface of the thin film and gaps are formed in the thin film to originate from valleys of the irregularities, the gaps may be formed in such a fashion that each columnar portion encompasses at least one projection of the irregularities on the thin film surface. The gaps may be formed in such a way that each columnar portion encompasses plural projections.

[0010] In the present invention, the gaps may be formed in the thin film during a first or subsequent charge-discharge cycle. Illustrating such a case, the thin film may be provided having irregularities on its surface before charge and discharge. On the first or subsequent charge-discharge cycle, the gaps are formed which originate from valleys of the irregularities on the thin film surface to divide the thin film into columns.

50 [0011] The irregularities on the thin film surface may be formed to substantially conform in shape to those on a surface of the underlying current collector. That is, the thin film when deposited on the irregularly surfaced current collector can have such irregularities thereon.

55 [0012] A surface roughness Ra (roughness average) of the current collector is preferably 0.01  $\mu\text{m}$  or larger, more preferably in the range of 0.01 - 1  $\mu\text{m}$ , most preferably in the range of 0.05 - 0.5  $\mu\text{m}$ . The surface roughness Ra, which is specified in Japanese Industrial Standards (JIS B 0601-1994), can be measured by a surface roughness meter, for example.

[0013] In the present invention, the surface roughness Ra of the current collector preferably satisfies the relationship

$Ra \leq t$ , where  $t$  is a thickness of the thin film of active material. It is also preferred that the surface roughness  $Ra$  of the current collector and the mean spacing of local peaks of profile  $S$  satisfy the relationship  $100Ra \geq S$ . The mean spacing of local peaks of profile  $S$ , which is specified in Japanese Industrial Standards (JIS B 0601-1994), can be measured by a surface roughness meter, for example.

[0014] The shape of the projections on the current collector surface is not particularly specified, but may preferably be substantially conical, for example.

[0015] Preferably, the projections have a round top which is suited to avoid localized current concentration during a charge-discharge reaction.

[0016] In the present invention, the gaps are formed in the thin film composed of active material to extend in its thickness direction. Such gaps may be formed on the first or subsequent charge-discharge cycle, or alternatively, preformed before charge and discharge. Illustrating one method of forming such gaps in the thin film before it is subjected to a charge-discharge process, the thin film of the electrode before being assembled into a battery is allowed to store and then release lithium or the like so that the thin film is made to expand and shrink in volume, thereby forming the gaps. In an exemplary case where lithium-free active material is used for a positive electrode, assembling may be performed with lithium being stored in the thin film. Also, the thin film divided by gaps into columns can be lithographically formed by utilizing a resist film patterned by photolithography.

[0017] The thin film of active material in accordance with the present invention can be formed from one or more materials capable of producing compounds or solid solutions with lithium, e.g. at least one selected from elements from Groups IIB, IIIB, IVB and VB of the periodic table and oxides and sulfides of transition metal elements from Periods 4, 5 and 6 of the periodic table.

[0018] In the present invention, examples of elements from Groups IIB, IIIB, IVB and VB of the periodic table that can produce compounds or solid solutions with lithium include carbon, aluminum, silicon, phosphorus, zinc, gallium, germanium, arsenic, cadmium, indium, tin, antimony, mercury, thallium, lead and bismuth. Specific examples of transition metal elements from Periods 4, 5 and 6 of the periodic table include scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, niobium, molybdenum, technetium, ruthenium, rhodium, palladium, silver, cadmium, lanthanum series elements, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold and mercury.

[0019] Preferred among the above-listed elements is at least one selected from carbon, silicon, germanium, tin, lead, aluminum, indium, zinc, cadmium, bismuth and mercury. Silicon and/or germanium is more preferred.

[0020] In general, silicon is roughly classified by its crystallinity into amorphous silicon, microcrystalline silicon, polycrystalline silicon and single crystal silicon. The term "noncrystalline silicon", as used herein, is meant to encompass amorphous silicon and microcrystalline silicon and exclude polycrystalline silicon and single crystal silicon. Silicon is identified as the amorphous silicon when Raman spectroscopy detects substantial absence of a peak around  $520\text{ cm}^{-1}$  which characterizes a crystalline region, and as the microcrystalline silicon when Raman spectroscopy detects the substantial presence of a peak around  $520\text{ cm}^{-1}$  corresponding to the crystalline region and a peak around  $480\text{ cm}^{-1}$  which indicates an amorphous region. Hence, the microcrystalline silicon consists substantially of a crystalline region and an amorphous region. Silicon is identified as the single crystal silicon or polycrystalline silicon when Raman spectroscopy detects substantial absence of a peak around  $480\text{ cm}^{-1}$  corresponding to the amorphous region.

[0021] In the present invention, the silicon thin film in the microcrystalline or amorphous form is preferably used for the thin film of active material.

[0022] In addition to the above-described silicon thin film, a germanium thin film or a silicon-germanium alloy thin film may also be preferably used for the thin film in the present invention. The germanium thin film in the amorphous or microcrystalline form is preferably used. The silicon-germanium alloy thin film in the microcrystalline or amorphous form is preferably used. The above-described procedure applied to the silicon thin film can be similarly used to determine the microcrystalline or amorphous nature of the germanium and silicon-germanium alloy thin films. Silicon and germanium, which can be mixed with each other to form a uniform solid solution, are found to provide good results in the present invention. It is accordingly believed that similar results are obtained with the use of their alloy, i.e., silicon-germanium alloy.

[0023] In the present invention, the thin film can be formed on the current collector by various methods which include, for example, CVD, sputtering, vapor evaporation, spraying and plating processes. Particularly preferred among such thin film forming methods are CVD, sputtering and vapor evaporation processes.

[0024] The current collector for use in the present invention is not particularly specified in type, so long as it assures good adhesion to the overlying thin film of active material. More specifically, the current collector may be comprised of at least one selected from copper, nickel, stainless steel, molybdenum, tungsten and tantalum, for example.

[0025] The current collector is preferably thin and thus preferably in the form of a metal foil. The current collector is preferably comprised of a material which does not form an alloy with lithium, particularly preferably of copper. The current collector is preferably in the form of a copper foil which is preferably roughened at its surface. A typical example of such a copper foil is an electrolytic copper foil. This electrolytic copper foil is obtained, for example, from an electrolyte

containing copper ions: A metallic drum is immersed in the electrolyte solution and rotated. The introduction of current results in the electrodeposition of copper on a surface of the drum. The electrolytic copper foil is then obtained by removing the deposited copper from the drum. The electrolytic copper foil may be subjected to surface roughening or other surface treatment at either one or both sides thereof.

5 [0026] As the current collector, a rolled copper foil, whose surface is roughened by depositing copper thereon via an electrolytic process, may be used.

[0027] Also, an interlayer may be provided between the current collector and the thin film of active material. In such an instance, the interlayer is preferably comprised of a material which contains a constituent easy to diffuse into the thin film. Preferred interlayer is a copper layer. Such a copper layer may be superimposed on a surface-roughened nickel foil (e.g., electrolytic nickel foil) to provide the current collector. Alternatively, copper may be deposited on a 10 nickel foil by an electrolytic process during which the nickel foil is roughened at its surface.

[0028] In this invention, the low-density regions may be preformed in the active thin film to extend in its thickness direction so that the gaps will be later formed along the low-density regions. Such low-density regions may be formed to extend upwardly from the valleys of irregularities on a surface of the current collector, for example.

15 [0029] In the present invention, it is preferred that the current collector constituent is diffused into the thin film of active material. The diffusion of the current collector constituent into the thin film improves adhesion between the current collector and the thin film. Where the diffusing current collector constituent is an element, such as copper, which does not form an alloy with lithium, the thin film in the diffusion region is less alloyed with lithium and undergoes less expansion and shrinkage during a charge-discharge reaction, so that a stress can be prevented from building up to the extent 20 that may cause the thin film to separate from the current collector.

[0030] Preferably, the concentration of the current collector constituent diffused into the thin film is higher in the vicinity of the current collector and lower at a location closer to the thin film surface. Due to the presence of such a concentration gradient of the current collector constituent, the thin film of active material is subjected to less expansion and shrinkage in the vicinity of the current collector during a charge-discharge reaction, so that a stress can be prevented from building up in the vicinity of the current collector to the extent that may cause the thin film to separate from the current collector. Also, the decreasing concentration of the current collector constituent toward the thin film surface enables a high charge-discharge capacity to remain.

25 [0031] It is preferred that the current collector constituent, when diffused into the thin film, forms a solid solution, instead of an intermetallic compound, with a component of the thin film. The intermetallic compound, as used herein, refers to a compound which has a specific crystal structure formed via combination of metals in specific proportions. The formation of solid solution, instead of intermetallic compound, of the thin film component and the current collector constituent improves adhesion between the thin film and the current collector, resulting in obtaining the increased charge-discharge capacity.

30 [0032] The thin film of active material in the present invention may be doped with an impurity. Examples of such impurities include elements of the periodic Groups IIIB, IVB, VB and VIB, such as phosphorus, aluminum, arsenic, antimony, boron, gallium, indium, oxygen and nitrogen.

[0033] Also, the thin film of active material in the present invention may be made up of a sequence of superimposed layers. These layers may differ from each other in terms of composition, crystallinity, impurity concentration or the like. Such layers may provide a thin film structure graded in its thickness direction. For example, such layers can provide 40 a thin film structure wherein the composition, crystallinity, impurity concentration or the like is varied in its thickness direction.

[0034] Preferably, the thin film of active material in the present invention stores lithium via formation of an alloy with lithium.

45 [0035] Lithium may be incorporated previously in the active thin film in the present invention. Lithium may be added during formation of the thin film of active material. That is, lithium may be introduced via formation of a lithium-containing thin film. Alternatively, lithium may be added or stored after formation of the thin film. One method is to use an electrochemical mechanism where lithium is added or stored in the thin film.

[0036] The thickness of the thin film of active material in the present invention is not particularly specified, but may be 20  $\mu\text{m}$  or below. It is preferably 1  $\mu\text{m}$  or above for the purpose of obtaining a high charge-discharge capacity.

50 [0037] In the present invention, an interlayer may be provided between the current collector and the thin film to improve adhesion therebetween. Preferably, such an interlayer may comprise a material which forms an alloy, more preferably a solid solution, with the current collector material and the active material.

[0038] The lithium battery of the present invention is characterized as including a negative electrode comprised of the above-described electrode of the present invention, a positive electrode and an electrolyte.

55 [0039] The term "lithium battery", as used herein, encompasses a lithium primary battery and a lithium secondary battery. Accordingly, the electrode of the present invention is applicable to lithium primary batteries as well as to lithium secondary batteries.

[0040] The rechargeable lithium battery (lithium secondary battery) of the present invention is characterized as in-

cluding a negative electrode comprised of the above-described electrode of the present invention, a positive electrode and a nonaqueous electrolyte.

**[0041]** An electrolyte solvent for use in the rechargeable battery of the present invention is not particularly limited in type but can be illustrated by a mixed solvent which contains cyclic carbonate such as ethylene carbonate, propylene carbonate or butylene carbonate and also contains chain carbonate such as dimethyl carbonate, methyl ethyl carbonate or diethyl carbonate. Also applicable is a mixed solvent of the above-listed cyclic carbonate and an ether solvent such as 1,2-dimethoxyethane or 1,2-diethoxyethane or a chain ester such as  $\gamma$ -butyrolactone, sulfolane or methyl acetate. Illustrative electrolyte solutes are  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)$ ,  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ ,  $\text{LiC}(\text{C}_2\text{F}_5\text{SO}_2)_3$ ,  $\text{LiAsF}_6$ ,  $\text{LiClO}_4$ ,  $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ ,  $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$  and mixtures thereof. Other applicable electrolytes include a gelled polymer electrolyte comprised of an electrolyte solution impregnated into a polymer electrolyte such as polyethylene oxide, polyacrylonitrile or polyvinylidene fluoride and inorganic solid electrolytes such as  $\text{LiI}$  and  $\text{Li}_3\text{N}$ , for example. The electrolyte for the rechargeable lithium battery of the present invention can be used without limitation, so long as an Li compound as its solute that imparts an ionic conductivity, as well as its solvent that dissolves and retains the Li compound, remain undecomposed at voltages during charge, discharge and storage of the battery.

**[0042]** Examples of positive active materials for the present invention include lithium-containing transition metal oxides such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiMnO}_2$ ,  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$  and  $\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$ ; lithium-free metal oxides such as  $\text{MnO}_2$ ; and the like. Other substances can also be used, without limitation, if they are capable of electrochemical insertion and release of lithium.

**[0043]** The electrode of the present invention is believed to be also useful for an electrode for nonaqueous electrolyte batteries and nonaqueous electrolyte rechargeable batteries which contain electrode active materials capable of storing and releasing alkaline metals other than lithium, such as sodium and potassium, and alkaline earth metals such as magnesium and calcium.

**[0044]** The electrode for use in rechargeable batteries, in accordance with another aspect of the present invention, is characterized as including an electrode material layer in the form of a thin film and a current collector adhered to the electrode material layer, wherein the thin film has low-density regions connected to each other like a network in a planar direction and extending in a thickness direction toward the current collector. Such an electrode for rechargeable batteries can be illustrated by the electrode for rechargeable lithium batteries, in accordance with the present invention, in its condition before the gaps are formed therein along the low-density regions to extend in its thickness direction.

**[0045]** It is accordingly preferred that a current collector constituent diffuses into the thin film. This diffused current collector constituent preferably forms a solid solution, instead of an intermetallic compound, with a component of the thin film, in the thin film.

**[0046]** Preferably, the thin film is formed on the current collector by a thin film-forming method. Examples of thin film-forming methods include CVD, sputtering, vapor evaporation, spraying and plating processes.

**[0047]** The low-density regions formed in the thin film are similar to those formed in the above-described electrode of the present invention for lithium batteries.

**[0048]** Also, the thin film and current collector used in the above-described electrode of the present invention for lithium batteries can be similarly used.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0049]**

Figure 1 is a schematic sectional view of a rechargeable lithium battery fabricated in Examples in accordance with the present invention;

Figure 2 is a photomicrograph (at a magnification of 2,000X) taken using a scanning electron microscope, showing an electrode in accordance with one embodiment of the present invention in its state before charge and discharge;

Figure 3 is a photomicrograph (at a magnification of 5,000X) taken using a scanning electron microscope, showing an electrode in accordance with one embodiment of the present invention in its state before charge and discharge;

Figure 4 is a photomicrograph (at a magnification of 500X) taken using a scanning electron microscope, showing an electrode in accordance with one embodiment of the present invention in its state after charges and discharges;

Figure 5 is a photomicrograph (at a magnification of 2,500X) taken using a scanning electron microscope, showing an electrode in accordance with one embodiment of the present invention in its state after charges and discharges;

Figure 6 is a photomicrograph (at a magnification of 1,000X) taken using a scanning electron microscope, showing a silicon thin film of an electrode in accordance with one embodiment of the present invention when viewed from above;

Figure 7 is a photomicrograph (at a magnification of 5,000X) taken using a scanning electron microscope, showing a silicon thin film of an electrode in accordance with one embodiment of the present invention when viewed from above;

Figure 8 is a photomicrograph (at a magnification of 1,000X) taken using a scanning electron microscope, showing a silicon thin film of an electrode in accordance with one embodiment of the present invention when viewed from a slight angle;

Figure 9 is a photomicrograph (at a magnification of 5,000X) taken using a scanning electron microscope, showing a silicon thin film of an electrode in accordance with one embodiment of the present invention when viewed from a slight angle;

Figure 10 is a schematic sectional view, showing a silicon thin film in the process of being divided by gaps into columns;

Figure 11 is a photomicrograph (at a magnification of 12,500X) taken using a transmission electron microscope, showing a section of a silicon thin film of an electrode a3 in accordance with the present invention;

Figure 12 is a photomicrograph (at a magnification of 25,000X) taken using a transmission electron microscope, showing a section of a silicon thin film of an electrode a6 in accordance with the present invention;

Figure 13 is a diagrammatic representation of the photomicrograph of Figure 11;

Figure 14 is a diagrammatic representation of the photomicrograph of Figure 12;

Figure 15 is a photomicrograph (at a magnification of 1,000X) taken using a scanning electron microscope, showing a silicon thin film surface of an electrode a3 in accordance with the present invention when viewed from above;

Figure 16 is a photomicrograph (at a magnification of 1,000X) taken using a scanning electron microscope, showing a silicon thin film surface of an electrode a6 in accordance with the present invention when viewed from above;

Figure 17 is a graphical representation illustrating concentration profiles of constituent elements in a silicon thin film of an electrode a6 in accordance with the present invention along the depth of the film;

Figure 18 is a schematic view, showing a construction of an apparatus which is employed when a thin film is formed by a vacuum vapor evaporation technique in examples of the present invention;

Figure 19 is a photomicrograph (at a magnification of 2,000X) taken using a scanning electron microscope, showing an electrode a7 in accordance with the present invention in its state before charge and discharge;

Figure 20 is a photomicrograph (at a magnification of 10,000X) taken using a scanning electron microscope, showing the electrode a7 in accordance with the present invention in its state before charge and discharge;

Figure 21 is a photomicrograph (at a magnification of 2,000X) taken using a scanning electron microscope, showing an electrode a8 in accordance with the present invention in its state before charge and discharge;

Figure 22 is a photomicrograph (at a magnification of 10,000X) taken using a scanning electron microscope, showing the electrode a8 in accordance with the present invention in its state before charge and discharge;

Figure 23 is a photomicrograph (at a magnification of 500X) taken using a scanning electron microscope, showing the electrode a7 in accordance with the present invention in its state after charges and discharges;

Figure 24 is a photomicrograph (at a magnification of 2,500X) taken using a scanning electron microscope, showing the electrode a7 in accordance with the present invention in its state after charges and discharges;

Figure 25 is a photomicrograph (at a magnification of 500X) taken using a scanning electron microscope, showing the electrode a8 in accordance with the present invention in its state after charges and discharges;

Figure 26 is a photomicrograph (at a magnification of 2,500X) taken using a scanning electron microscope, showing the electrode a8 in accordance with the present invention in its state after charges and discharges;

Figure 27 is a photomicrograph (at a magnification of 1,000X) taken using a scanning electron microscope, showing a germanium thin film of the electrode a7 in accordance with the present invention in its state after charges and discharges, when viewed from above;

Figure 28 is a photomicrograph (at a magnification of 5,000X) taken using a scanning electron microscope, showing a germanium thin film of the electrode a7 in accordance with the present invention in its state after charges and discharges, when viewed from above;

Figure 29 is a photomicrograph (at a magnification of 1,000X) taken using a scanning electron microscope, showing a germanium thin film of the electrode a7 in accordance with the present invention in its state after charges and discharges, when viewed from a slight angle;

Figure 30 is a photomicrograph (at a magnification of 5,000X) taken using a scanning electron microscope, showing a germanium thin film of the electrode a7 in accordance with the present invention in its state after charges and discharges, when viewed from a slight angle;

Figure 31 is a photomicrograph (at a magnification of 1,000X) taken using a scanning electron microscope, showing a germanium thin film of the electrode a8 in accordance with the present invention in its state after charges and discharges, when viewed from above;

Figure 32 is a photomicrograph (at a magnification of 5,000X) taken using a scanning electron microscope, showing a germanium thin film of the electrode a8 in accordance with the present invention in its state after charges and discharges, when viewed from above;

Figure 33 is a photomicrograph (at a magnification of 1,000X) taken using a scanning electron microscope, showing a germanium thin film of the electrode a8 in accordance with the present invention in its state after charges and



discharges, when viewed from a slight angle;

Figure 34 is a photomicrograph (at a magnification of 5,000X) taken using a scanning electron microscope, showing a germanium thin film of the electrode a8 in accordance with the present invention in its state after charges and discharges, when viewed from a slight angle;

Figure 35 is a photomicrograph (at a magnification of 1,000X) taken using a scanning electron microscope, showing a germanium thin film of the electrode a7 in accordance with the present invention in its state before charge and discharge, when viewed from above;

Figure 36 is a photomicrograph (at a magnification of 1,000X) taken using a scanning electron microscope, showing a germanium thin film of the electrode a8 in accordance with the present invention in its state before charge and discharge, when viewed from above;

Figure 37 is a graphical representation illustrating concentration profiles of constituent elements in a germanium thin film of the electrode a7 in accordance with the present invention along the depth of the film;

Figure 38 is a graphical representation, illustrating concentration profiles of constituent elements in a germanium thin film in the electrode a8 in accordance with the present invention along the depth of the film;

Figure 39 is a photomicrograph (at a magnification of 2,000X) taken using a scanning electron microscope, showing a section of an electrode a-11 in accordance with the present invention before charge and discharge;

Figure 40 is a photomicrograph (at a magnification of 10,000X) taken using a scanning electron microscope, showing a section of the electrode a-11 in accordance with the present invention before charge and discharge;

Figure 41 is a photomicrograph (at a magnification of 1,000X) taken using a scanning electron microscope, showing a silicon thin film of the electrode a-11 in accordance with the present invention before charge and discharge, when viewed from above;

Figure 42 is a photomicrograph (at a magnification of 1,000X) taken using a scanning electron microscope, showing a silicon thin film of the electrode a-11 in accordance with the present invention after charges and discharges, when viewed from above;

Figure 43 is a photomicrograph (at a magnification of 500,000X) taken using a transmission electron microscope, showing an interface between a copper foil and a silicon thin film and its vicinities;

Figure 44 is a photomicrograph (at a magnification of 1,000,000X) taken using a transmission electron microscope, showing an interface between a copper foil and a silicon thin film and its vicinities;

Figure 45 is a graphical representation, illustrating concentration profiles of copper and hydrogen in a mixed layer in an electrode c1 along the depth of the layer; and

Figure 46 is a graphical representation, illustrating concentration profiles of copper and hydrogen in a mixed layer in an electrode c3 along the depth of the layer.

## BEST MODE FOR CARRYING OUT THE INVENTION

[0050] The present invention is below described in more detail by way of examples. It will be recognized that the following examples merely illustrate the practice of the present invention but are not intended to be limiting thereof. Suitable changes and modifications can be effected without departing from the scope of the present invention.

### (EXPERIMENT 1)

#### (Fabrication of Negative Electrode)

[0051] A microcrystalline silicon thin film was formed on a rolled copper foil (18  $\mu\text{m}$  thick) by a CVD method, using the rolled copper foil as a substrate, silane ( $\text{SiH}_4$ ) as a source gas and a hydrogen gas as a carrier gas. Specifically, the copper foil as a substrate was placed on a heater within a reaction chamber. An interior of the reaction chamber was evacuated by a vacuum evacuator to a pressure of 1 Pa or lower. The silane gas as a source gas and the hydrogen ( $\text{H}_2$ ) gas as a carrier gas were introduced via a source gas inlet port. The substrate was heated to 180 °C on the heater. A degree of vacuum was adjusted by the vacuum pumping apparatus to a reaction pressure. An RF power supply was operated to excite a radio frequency wave which is introduced via an electrode to induce a glow discharge. Detailed thin-film forming conditions are listed in Table 1. In Table 1, a volumetric unit, sccm, indicates a volumetric flow rate ( $\text{cm}^3/\text{minute}$ ) of a fluid at 0 °C at 1 atmospheric pressure (101.33 kPa) per minute and is an abbreviation of standard cubic centimeters per minute.

Table 1

Conditions	During Film Formation
Source Gas (SiH <sub>4</sub> ) Flow Rate	10sccm
Carrier Gas (H <sub>2</sub> ) Flow Rate	200sccm
Substrate Temperature	180°C
Reaction Pressure	40Pa
RF Power	555W

[0052] The microcrystalline silicon thin film was deposited under the above-specified conditions to a thickness of about 10  $\mu\text{m}$ . Observation by an electron microscope (at 2,000,000X magnification) ascertained noncrystallinity of the thin film in the way that an amorphous region was arranged to surround a crystalline region consisting of microfine crystal grains. A 17 mm diameter piece was punched out from the resulting sample to provide an electrode a1. A piece identical to the electrode a1 was subjected to heat treatment at 400 °C for 3 hours to provide an electrode a2.

[0053] For comparative purposes, 90 parts by weight of commercially available single crystal silicon powder (particle diameter of 10  $\mu\text{m}$ ) and 10 parts by weight of polytetrafluoroethylene as a binder were mixed. This mixture was pressed in a 17 mm diameter mold to obtain a pellet-form electrode b1.

(Fabrication of Positive Electrode)

[0054] Starting materials, Li<sub>2</sub>CO<sub>3</sub> and CoCO<sub>3</sub>, were weighed such that the atomic ratio of Li and Co, Li:Co, was brought to 1:1, and then mixed in a mortar. The mixture was pressed in a 17 mm diameter mold and calcined in the air at 800 °C for 24 hours to obtain a calcined product consisting of LiCoO<sub>2</sub>. This was subsequently ground into particles with a mean particle diameter of 20  $\mu\text{m}$ .

[0055] 80 parts by weight of the resulting LiCoO<sub>2</sub> powder, 10 parts by weight of acetylene black as a conducting material and 10 parts by weight of polytetrafluoroethylene as a binder were mixed. The mixture was pressed in a 17 mm diameter mold to obtain a pellet-form positive electrode.

(Preparation of Electrolyte Solution)

[0056] 1 mole/liter of LiPF<sub>6</sub> was dissolved in a mixed solvent containing equi-volumes of ethylene carbonate and diethyl carbonate to prepare an electrolyte solution for use in the following battery construction.

(Construction of Battery)

[0057] A coin type rechargeable lithium battery was constructed using the above-fabricated electrode a1, a2 or b1 for the negative electrode, and the above-fabricated positive electrode and the above-prepared electrolyte solution.

[0058] Figure 1 is a schematic sectional view, illustrating a such-constructed rechargeable lithium battery which includes a positive electrode 1, a negative electrode 2, a separator 3, a positive can 4, a negative can 5, a positive current collector 6, a negative current collector 7 and an insulating gasket 8 made of polypropylene.

[0059] The positive electrode 1 and negative electrode 2 are disposed on opposite sides of the separator 3. These are enclosed in a battery case composed of the positive can 4 and negative can 5. The positive electrode 1 is connected to the positive can 4 by the positive current collector 6. The negative electrode 2 is connected to the negative can 5 by the negative current collector 7. Such construction enables charge and discharge as a secondary battery.

[0060] As a result, batteries A1, A2 and B1 were constructed using the electrodes a1, a2 and b1 for the negative electrode, respectively.

(Measurement of Charge-Discharge Cycle Life Characteristics)

[0061] Each battery, excepting the battery B1, was charged at a current of 100  $\mu\text{A}$  at 25 °C until a negative electrode capacity reached 2,000 mAh/g, and then discharged. This was recorded as a unit charge-discharge cycle. Cycling was effected to measure a 50th-cycle capacity retention rate for each battery. The battery B1, which could not be charged to 2,000 mAh/g, was subjected to a cycle test wherein it was charged to 4.2 V and then discharged. The results are given in Table 2.

[0062] In Table 2, a hydrogen concentration obtained from SIMS measurement, a ratio of peak intensities around

480  $\text{cm}^{-1}$  and 520  $\text{cm}^{-1}$  as determined by Raman spectral analysis, and a crystal grain size calculated from an X-ray diffraction spectrum and the Scherrer's equation, all for the negative active material of each battery, are also given. Also, the crystal grain size of the negative active material of the battery B1 is given by the particle diameter of the powder since both are considered to be almost equal in value to each other.

Table 2

Battery	50th-Cycle Capacity Retention Rate	Hydrogen Content	Ratio of Peak Intensities Intensities (480 $\text{cm}^{-1}$ /520 $\text{cm}^{-1}$ )	Crystal Grain Size
A1	85%	4%	0.1	1nm
A2	78%	0.01%	0.1	1nm
B1	5%	0%	0	10 $\mu\text{m}$

[0063] As can be clearly seen from the results shown in Table 2, the batteries A1 and A2 in accordance with the present invention both exhibit markedly higher capacity retention rates compared to the comparative battery B1.

[0064] As such, the use of the microcrystalline silicon thin film for the negative active material results in the marked improvement of charge-discharge cycle characteristics of the rechargeable lithium battery. This is believed due to the following reason: In the microcrystalline silicon thin film, the moderation of expansion and shrinkage which occurs when lithium is stored and released prevents the negative active material from being pulverized and thereby suppresses the possible reduction of current collecting capability.

#### (EXPERIMENT 2)

[0065] The procedure used in Experiment 1 to construct the battery A1 was followed, except that an electrolytic copper foil (18  $\mu\text{m}$  thick) was used for the current collector as a substrate. That is, a microcrystalline silicon thin film (about 10  $\mu\text{m}$  thick) was deposited on the electrolytic copper foil to fabricate an electrode a3. Using this electrode, a battery A3 was constructed.

[0066] Also, the rolled copper foil used in Experiment 1 was subjected to a one-minute grinding treatment with a #400 or #120 emery paper to provide a ground copper foil. The procedure used in Experiment 1 to construct the battery A1 was followed, except that such a ground copper foil was used for the current collector as a substrate. That is, a microcrystalline silicon thin film (about 10  $\mu\text{m}$  thick) was deposited on the copper foil to fabricate an electrode. The electrode fabricated using the copper foil ground with a #400 emery paper was designated as an electrode a4 and the electrode fabricated using the copper foil ground with a #120 emery paper was designated as an electrode a5. These electrodes were used to construct batteries A4 and A5 in the same manner as in Experiment 1.

[0067] These batteries A3 - A5 and the batteries A1 and B1 constructed in Experiment 1 were subjected to a charge-discharge cycle test under the same conditions used in Experiment 1 to obtain a 10th-cycle capacity retention rate for each. The results are given in Table 3. Also given in Table 3 are a surface roughness Ra and a mean spacing of local peaks S for the copper foil, as a current collector, of each of the batteries A1, B1 and A3 - A5.

[0068] The surface roughness Ra and the mean spacing of local peaks S for each copper foil were measured using a stylus profiler Dektak ST (available from ULVAC Inc.) with a scanning distance of 2.0 mm. The surface roughness Ra was calculated after correction of a deflection portion. The deflection portion was collected using the correction values with a low pass = 200  $\mu\text{m}$  and a high pass = 20  $\mu\text{m}$ . The surface roughness Ra was automatically calculated and the mean spacing of local peaks S was read from the chart.

Table 3

Battery	10th-Cycle Capacity Retention Rate	Current Collector (Copper Foil)	
		Surface Roughness Ra ( $\mu\text{m}$ )	Mean Spacing S ( $\mu\text{m}$ )
A1	97%	0.037	14
A3	99%	0.188	11
A4	98%	0.184	9
A5	99%	0.223	8
B1	20%	0.037	14

[0069] As can be clearly seen from the results given in Table 3, the batteries A3 - A5 using the copper foils with higher values of surface roughness Ra for the current collector exhibit improved 10th-cycle capacity retention rates compared to the battery A1 using the copper foil with the lowest value of surface roughness Ra. This is considered due to the following reason: The copper foil with a higher value of surface roughness Ra, when used for the current collector, improves adhesion between the current collector and the active material. This adhesion improvement reduces the influence of structural change, such as falling-off of the active material that occurs when it expands or shrinks during storage or release of lithium.

#### (EXPERIMENT 3)

[0070] The batteries A1 and A3 respectively constructed in Experiments 1 and 2 were further subjected to a charge-discharge cycle test under the same test conditions as used in the Experiment 1 to measure a 30th-cycle capacity retention rate. The results are shown in Table 4.

Table 4

Battery	30th-Cycle Capacity Retention Rate
A1	91%
A3	97%

[0071] As can be clearly seen from the results given in Table 4, the batteries A1 and A3 exhibit good capacity retention rates even on the 30th-cycle. Particularly, the battery A3 using the copper foil with a higher value of surface roughness Ra for the current collector exhibits good capacity retention rate.

[0072] The electrode a3 incorporated in the battery A3 was viewed under an electron microscope to observe a condition of its silicon thin film. First, the electrode a3 in its state prior to being incorporated in the battery, i.e., before charge and discharge, was observed using a scanning electron microscope. Figures 2 and 3 are photomicrographs (secondary electron images) taken with a scanning electron microscope, both showing the electrode a3 in its state before charge and discharge. Figures 2 and 3 are taken at 2,000X and 5,000X magnifications, respectively.

[0073] The electrode was embedded in a resin and then sliced to provide a sample. The layers of the embedding resin are found in upper and lower end portions of Figure 2 and in an upper end portion of Figure 3.

[0074] In Figures 2 and 3, a portion that appears slightly light indicates the copper foil. The deposited silicon thin film (about 10  $\mu\text{m}$  thick) is found as a dark portion on the copper foil. As shown in Figures 2 and 3, irregularities are formed on a surface of the copper foil. Particularly, projections have a generally conical shape. Similar irregularities are formed on a surface of the silicon thin film deposited on the copper foil. Accordingly, the surface irregularities of the silicon thin film appear to generally conform in shape to those formed on the copper foil surface.

[0075] Next, the electrode a3 was removed from the battery A3 after 30 cycles, embedded in a resin, and then subjected to observation under a scanning electron microscope in the same manner as described previously. Here, the electrode a3 was removed after discharge. Thus, the observed electrode a3 was in its state after discharge.

[0076] Figures 4 and 5 are photomicrographs (secondary electron images) taken with a scanning electron microscope, each showing the electrode a3 after discharge. Figures 4 and 5 are taken at 500X and 2,500X magnifications, respectively.

[0077] As shown in Figures 4 and 5, the silicon thin film has gaps that extend in its thickness direction and divide the silicon thin film into columns. Gaps are barely found to extend in a planar direction. A bottom of each columnar portion is found to adhere well to the copper foil as a current collector. Also, each columnar portion has a round top. It is thus understood that these gaps are formed to originate from the valleys of irregularities that were found on the surface of the silicon thin film in its state before charge and discharge.

[0078] Further, the surface of the silicon thin film of the electrode a3 after charges and discharges was observed with a scanning electron microscope. Figures 6 and 7 are photomicrographs (secondary electron images) taken with a scanning electron microscope, each showing the surface of the silicon thin film when viewed from above. Figures 6 and 7 are taken at 1,000X and 5,000X magnifications, respectively. Figures 8 and 9 are photomicrographs (secondary electron images) taken with a scanning electron microscope, each showing the surface of the silicon thin film when viewed at a slight angle. Figures 8 and 9 are taken at 1,000X and 5,000X magnifications, respectively.

[0079] As shown in Figures 6 - 9, the gaps are formed in such a way to surround the columnar portions of the silicon thin film so that spaces are defined between neighboring columnar portions. When the silicon thin film stores lithium on charge, the columnar portions will expand and increase in volume. This increment in volume, however, is believed to be accommodated by those spaces provided around the columnar portions. On discharge, the columnar portions of the silicon thin film release the lithium and shrink to decrease in volume. This decrement in volume is believed to

restore the spaces around the columnar portions. Such a columnar structure of the silicon thin film is effective to relax a stress caused by expansion and shrinkage of the active material on charge and discharge, so that falling-off of the active silicon thin film from the current collector can be prevented.

[0080] The formation of the gaps which divide the silicon thin film into columns results in a marked increase in contact area thereof with the electrolyte solution. Also, the columnar portions are almost comparable in size to each other. These are believed to allow efficient occurrence of a charge-discharge reaction accompanying storage and release of lithium in the thin film of active material.

[0081] Since the individual columnar portions of the silicon thin film adhere to the current collector, as shown in Figures 4 and 5, good electrical connection is provided between the active material and the current collector. This is believed to allow efficient occurrence of the charge-recharge reaction.

[0082] As also shown in Figures 6 - 9, each columnar portion has a round top. This provides an electrode structure which prevents localized current concentration and reduces the occurrence such as of a deposition reaction of a lithium metal.

[0083] Figure 10 is a schematic sectional view, illustrating a process whereby the silicon thin film deposited on a copper foil is divided into columns by the gaps formed therein.

[0084] As shown in Figure 10(a), the copper foil 10 has irregularities on its surface 10a. The copper foil with the increased value for surface roughness Ra has the larger irregularities.

[0085] Figure 10(b) illustrates a noncrystalline silicon thin layer 11 deposited on a rough surface 10a of the copper foil 10. The surface 11a of the silicon thin film 11 is influenced by the irregularities on the surface 10a of the copper foil 10 to have similar irregularities. Before charge and discharge, the silicon thin film 11 remains undivided, as shown in Figure 10(b). When charging is effected, the silicon thin film 11 stores lithium therein and expands in volume. During the charge, the silicon thin film 11 appears to expand in both thickness and planar directions of the thin film, although the detail is not clear. During the subsequent discharge reaction, the silicon thin film 11 releases lithium therefrom and shrinks in volume. At this time, a tensile stress is produced in the silicon thin film 11. Probably, such a stress concentrates at valleys 11b of the irregularities on the surface 11a of the silicon thin film 11 to result in the formation of gaps 12 that originate from the valleys 11b and extend in the thickness direction, as shown in Figure 10(c). Conceivably, the gaps 12 such formed relax the stress to allow the silicon thin film 11 to shrink without occurrence of falling-off from the copper foil 10.

[0086] In the silicon thin film divided into columns in the fashion as described above, the spaces provided around the columnar portions serve to relax the stress resulting from expansion and shrinkage of the active material during the succeeding charge-discharge cycles. This appears to assure repetitive charge-discharge cycling while preventing falling-off of the active material from the current collector.

[0087] Further, the electrode a3 incorporating an about 10  $\mu\text{m}$  thick, microcrystalline silicon thin film deposited on an electrolytic copper foil was observed under a transmission electron microscope to study a mechanism whereby the gaps are formed in the silicon thin film. Figure 11 is a photomicrograph (at a magnification of 12,500X) taken with a transmission electron microscope, showing a section of the electrode a3 before charge and discharge. The observation sample was prepared by slicing the resin-embedded electrode.

[0088] Figure 13 is a diagrammatic representation of the photomicrograph of Figure 11. In the photomicrograph of Figure 11 taken with a transmission electron microscope, the silicon thin film 11 is deposited on the surface 10a of the electrolytic copper foil 10, as diagrammatically shown in Figure 13. The silicon thin film 11 appears light relative to the copper foil 10 in the photomicrograph taken with a transmission electron microscope. In the silicon thin film shown in Figure 11, light portions are observed in the regions extending between respective valleys 11b and 10b of the irregularities on the surfaces 11a and 10a of the silicon thin film 11 and copper foil 10. These light portions are indicated by single-dotted chain lines A, B and C in Figure 13. Particularly, the light portion is observed more clearly in the region indicated by A. These regions are considered to be low in density, i.e., low-density regions of the silicon thin film 11. For the purpose of observing such low-density regions in more detail, an electrode a6 was fabricated by depositing an about 2  $\mu\text{m}$  thick, microcrystalline silicon thin film on an electrolytic copper foil under the same conditions as used in the fabrication of the electrode a3.

[0089] Figure 12 is a photomicrograph taken by a transmission electron microscope, showing the electrode a6 when observed in the same manner as described above. Figure 12 is taken at a magnification of 25,000X. Figure 14 is a diagrammatic representation of the photomicrograph of Figure 12. As clear from Figure 12, a low-density region is also observed in the region D of the electrode a6 that extends between the respective valleys 11b, 10b of the irregularities on the surfaces 11a, 10a of the silicon thin film 11 and the copper foil 10. A detailed observation of the photomicrograph of Figure 12 reveals a number of fine lines extending in directions shown by the arrows in Figure 14. It seems very likely that such lines are formed as the silicon thin film grows. It accordingly appears that the silicon thin film 11 grows generally perpendicularly to the surface 10a of the copper foil 10. It also appears that the silicon thin film layer grows in such a direction to collide at the region D with an adjacent silicon thin film layer being deposited and growing on the adjacent inclined surface of the copper foil. Thus the formation of the low-density region D is very likely to have resulted

from such a collision at the region D. It also appears that the collision of the silicon thin film layers with each other is continued till the end of thin film formation, and formation of the low-density region also continues until reaching the surface of the silicon thin film.

[0090] Figure 15 is a photomicrograph (secondary electron image) taken with a scanning electron microscope, showing a surface of a silicon thin film of an electrode a3 when observed from above. The electrode a3 shown in Figure 15 is in its state before charge and discharge. Figure 15 is viewed at 1,000X magnification. In Figure 15, portions appearing lightened indicate projections on a surface of the silicon thin film and the surrounding portions appearing darkened indicate valleys on the surface of the silicon thin film. As shown in Figure 15, the valleys on the surface of the silicon thin film are connected to each other like a network. It is accordingly found that the low-density regions define a continuous network in a plane of the silicon thin film. As shown in Figures 11 and 13, such a reticulated low-density region also extends in a thickness direction toward the current collector. The dark portions in Figure 15 do not indicate the gaps (spaces). This is apparent from the fact that no gap (space) is observed which extends in the thickness direction of the thin film in the photomicrographs of Figures 2 and 3 taken by a scanning electron microscope.

[0091] Figure 16 is a photomicrograph (secondary electron image) taken at a magnification of 1,000 using a scanning electron microscope, showing a surface of a silicon thin film, when observed from above, of an electrode a6 in its state before charge and discharge. As apparent from Figure 16, the valleys in the electrode a6 are also connected to each other like a network. It is accordingly found that the low-density regions are arranged like a network continuous in a planar direction.

[0092] Figure 17 is a graph showing concentration profiles of constituent elements along the thickness of the silicon thin film in the electrode a6. The concentration profiles of constituent elements were obtained via measurement of concentrations of copper ( $^{63}\text{Cu}^+$ ) and silicon ( $\text{Si}^{2+}$ ) by SIMS using  $\text{O}_2^+$  as a sputtering source. In Figure 17, the abscissa indicates a depth ( $\mu\text{m}$ ) from a surface of the silicon thin film and the ordinate indicates an intensity (count) of each constituent element.

[0093] As apparent from Figure 17, a constituent element of the current collector, copper (Cu), is found to diffuse in the silicon thin film at locations adjacent to the current collector. The copper (Cu) concentration decreases at a location closer to the surface of the silicon thin film. The copper (Cu) concentration is also found to vary in a continuous fashion. This demonstrates that a solid solution of silicon and copper, instead of an intermetallic compound thereof, is formed in the copper(Cu)-diffused region.

[0094] In view of the previous discussion, the following is very likely to explain a mechanism whereby the gaps are formed in the silicon thin film to extend in its thickness direction as it expands and shrinks during charge and discharge. That is, a stress caused by expansion or shrinkage in volume of the silicon thin film concentrates at valleys of the irregularities on the silicon thin film surface, as previously explained by referring to Figure 10. Also, in the silicon thin film, there initially exists low-density regions which are relatively low in mechanical strength, extending from the valleys toward the current collector. As the result of the above-mentioned situations, the gaps (spaces) are likely to be formed along these low-density regions.

[0095] Also, as shown in Figure 17, the diffusion of copper, a constituent element of the current collector, into the silicon thin film creates a concentration gradient of copper therein, so that the copper concentration is higher at a location closer to the current collector and lower at a location closer to the surface of the silicon thin film. Accordingly, a higher concentration of copper nonreactive with lithium and a lower concentration of silicon reactive with lithium exist at a location closer to the current collector. In the vicinity of the current collector, the silicon thin film is believed to store and release less lithium, undergo less expansion and shrinkage, and thus produce a lower level of stress which leads to the reduced formation of the gaps (spaces) which may occasion separation or removal of the silicon thin film from the current collector. As a result, the bottoms of the columnar portions of the silicon thin film can be kept adherent to the current collector.

[0096] The silicon thin film divided by such gaps into columns keeps a strong adhesion to the current collector even during charge-discharge cycles. Also, the spaces provided to surround the columnar portions serve to relax the stress caused by expansion and shrinkage of the thin film that occur with charge-discharge cycling. These are believed to be contributors to excellent charge-discharge cycle characteristics.

#### (EXPERIMENT 4)

##### (Fabrication of Electrode a7)

[0097] An electrolytic copper foil similar to that for use in the fabrication of the electrode a3 was used for a current collector as a substrate. An amorphous germanium thin film (about 2  $\mu\text{m}$  thick) was formed on this copper foil by an RF sputtering technique to fabricate an electrode a7.

[0098] The thin film was formed using germanium as a target, at a sputtering gas (Ar) flow rate of 100 sccm, an ambient substrate temperature (not heated), a reaction pressure of 0.1 Pa, and 200 W RF power.

[0099] The resulting germanium thin film was analyzed by Raman spectroscopy which detected the presence of a peak around  $274\text{ cm}^{-1}$  and the absence of a peak around  $300\text{ cm}^{-1}$ . This revealed an amorphous nature of the germanium thin film.

#### 5 (Fabrication of Electrode a8)

[0100] An amorphous germanium thin film (about  $2\text{ }\mu\text{m}$  thick) was formed on an electrolytic copper foil, similar in type to the current collector of the electrode a7, by using a vapor evaporation technique to fabricate an electrode a8.

[0101] Specifically, the germanium thin film was deposited on the substrate by utilizing an apparatus of the construction shown in Figure 18. Referring to Figure 18, an ECR plasma source 21 includes a plasma generation chamber 22 to which a microwave power 25 and an Ar gas 26 are supplied. An Ar plasma is generated when the microwave power 25 is supplied to the plasma generation chamber 22. This Ar plasma 23 is directed to exit from the plasma generation chamber 22 and bombard a substrate 20. The germanium thin film can be deposited on the substrate 20 by utilizing an electron beam from an electron beam (EB) gun disposed below the substrate 20.

[0102] The electrolytic copper foil substrate was pretreated by Ar plasma irradiation before the germanium thin film was deposited thereon. A degree of vacuum within the reaction chamber was adjusted to about  $0.05\text{ Pa}$  (about  $5 \times 10^{-4}\text{ Torr}$ ). The substrate was exposed to the Ar plasma under conditions of an Ar gas flow rate of  $40\text{ sccm}$  and a supplied microwave power of  $200\text{ W}$ . During the Ar plasma irradiation, an bias voltage of  $-100\text{ V}$  was applied to the substrate. The pretreatment was accomplished by exposing the substrate to the Ar plasma for 15 minutes.

[0103] Next, the germanium thin film was deposited at a deposition rate of  $1\text{ nm/sec}$  ( $10\text{ }\text{\AA}/\text{sec}$ ) using an electron beam gun. The substrate temperature was ambient temperature (not heated).

[0104] The resulting germanium thin film was analyzed by Raman spectroscopy which revealed an amorphous nature of the germanium thin film, as similar to the electrode a7.

#### 25 (Fabrication of Electrode b2)

[0105] 80 parts by weight of germanium powder with a mean particle diameter of  $10\text{ }\mu\text{m}$ , 10 parts by weight of acetylene black as an electroconductive material, and 10 parts by weight of polytetrafluoroethylene as a binder were mixed. This mixture was pressed in a  $17\text{ mm}$  diameter mold to fabricate a pellet-form electrode b2.

#### 30 (Construction of Batteries)

[0106] The procedure of Experiment was repeated, except that the above-fabricated electrodes a7, a8 and b2 were used for the negative electrode, to construct batteries A7, A8 and B2.

#### 35 (Evaluation of Charge-Discharge Cycle Characteristics)

[0107] Each battery was charged at a current of  $0.1\text{ mA}$  at  $25\text{ }^{\circ}\text{C}$  to  $4.2\text{ V}$ , and then discharged to  $2.75\text{ V}$ . This standard charge-discharge cycling was repeated to measure a capacity retention rate on the 10th cycle. The measurement results are given in Table 5.

Table 5

Battery	10th-Cycle Capacity Retention Rate
A7	96%
A8	93%
B2	39%

[0108] As apparent from Table 5, the batteries A7 and A8 using the electrodes in accordance with this invention, i. e., the electrodes incorporating the germanium thin film formed on the current collector, for the negative electrode exhibit markedly improved capacity retention rates compared to the battery B2 using the germanium powder for the negative electrode.

#### 55 (Observation With Electron Microscope)

[0109] Figures 19 and 20 are photomicrographs (reflection electron images) taken with a scanning electron microscope, each showing a section of the electrode a7 in its state before being charged and discharged. Figures 19 and

20 were taken at magnifications of 2,000X and 10,000X, respectively.

[0110] Each electrode was resin embedded and then sliced to provide a sample. The embedding resin is observed as layers located in upper and lower end portions of Figure 19 and in an upper end portion of Figure 20.

[0111] In Figures 19 and 20, the copper foil and the germanium thin film appear lightened relative to the rest. A thin layer overlying the copper foil is the germanium thin film. Irregularities are defined on a surface of the copper foil. Similar irregularities are also found on a surface of the germanium thin film. This suggests that the irregularities on the germanium thin film surface were formed to conform in shape to those defined on the copper foil surface.

[0112] In Figure 20, there is observed a dark portion that is located in a germanium thin film region overlying a leftmost valley of the copper foil and extends in a thickness direction of the thin film. This portion is very likely to indicate a region of low density, i.e., a low-density region of the germanium thin film.

[0113] Figures 21 and 22 are photomicrographs (reflection electron images) taken with a scanning electron microscope, each showing a section of the electrode a8 in its state before being charged and discharged. Figures 21 and 22 are taken at magnifications of 2,000X and 10,000X, respectively. Like the electrode a7 shown in Figures 19 and 20, a sample of this electrode is embedded in a resin.

[0114] In Figures 21 and 22, a lightened portion indicates a copper foil and a slightly darker portion carried thereon is a germanium thin film (about 2  $\mu\text{m}$  thick). Irregularities are defined on both surfaces of the germanium thin film and the copper foil of the electrode a8, as analogous to the electrode a7.

[0115] Figures 23 and 24 are photomicrographs (reflection electron images) taken with a scanning electron microscope, each showing a section of the electrode a7 removed from the battery A7 after 10 cycles. Figures 25 and 26 are photomicrographs (reflection electron images) taken with a scanning electron microscope, each showing a section of the electrode a8 removed from the battery A8 after 10 cycles. In either case, the electrode was resin embedded and then sliced to provide a sample. Figures 23 and 25 are both taken at a magnification of 500X. Figures 24 and 26 are both taken at a magnification of 2,500X.

[0116] In Figures 23 - 26, a portion which appears white on the surface of the germanium thin film is gold coated thereon before it is embedded in a resin. The coating of gold is provided to prevent any reaction which may occur between the germanium thin film and the resin and also define a clear boundary therebetween.

[0117] As can be clearly seen from Figures 23 - 26, charge-discharge cycling causes formation of gaps which extend in a thickness direction of the germanium thin film and divide the thin film into columns, as similar to the case of the silicon thin film. Although a small difference in contrast between the copper foil, as a current collector, and the germanium thin film makes it difficult to distinguish a boundary therebetween, the careful observation reveals the presence of columnar portions of the germanium thin film over projections of the current collector and thus good adhesion of the germanium thin film to the current collector.

[0118] Unlike the case of silicon thin film, laterally-extending gaps are also observed in the germanium thin film. It is very likely, however, that such gaps were formed when the germanium thin film was polished before proceeding to sectional observation.

[0119] Also, the width of a gap (space) between neighboring columnar portions is found to be larger in the germanium thin film than in the silicon thin film. After charge-discharge cycling, the height of the columnar portions measured about 6  $\mu\text{m}$ , which is about three times the initial film thickness of the germanium thin film, 2  $\mu\text{m}$ , before the charge-discharge cycling. This is considered to indicate that when the thin film shrinks on discharge after it has expanded due to storage of lithium during charge, the shrinkage occurs mainly in a lateral direction, i.e., in a planar direction. It is accordingly believed that the wide gaps (spaces) between the columnar portions result from a small percent shrinkage of the germanium thin film in its thickness direction.

[0120] Figures 27 and 28 are photomicrographs (secondary electron images) taken with a scanning electron microscope, each showing a germanium thin film of the electrode a7 in its state after charges and discharges, when observed from above. Figures 27 and 28 are taken at magnifications of 1,000X and 5,000X, respectively. Figures 29 and 30 are photomicrographs (secondary electron images) taken with a scanning electron microscope, each showing the germanium thin film of the electrode a7 in its state after charges and discharges, when observed at a slight angle. Figures 29 and 30 are taken at magnifications of 1,000X and 5,000X, respectively.

[0121] Figures 31 and 32 are photomicrographs (secondary electron images) taken with a scanning electron microscope, each showing a germanium thin film of the electrode a8 in its state after charges and discharges, when observed from above. Figures 31 and 32 are taken at magnifications of 1,000X and 5,000X, respectively. Figures 33 and 34 are photomicrographs (secondary electron images) taken with a scanning electron microscope, each showing the germanium thin film of the electrode a8 in its state after charges and discharges, when observed at a slight angle. Figures 33 and 34 are taken at magnifications of 1,000X and 5,000X, respectively.

[0122] As shown in Figures 27 - 34, gaps (spaces) are formed in such a fashion to surround the columnar portions of the germanium thin film to thereby define spaces between the neighboring columnar portions. It is believed that these spaces serve to relax the stress caused by expansion and shrinkage of the active material during charge and discharge, as also described in the previous case of silicon thin film.



[0123] Figures 35 is a photomicrograph (secondary electron images) taken with a scanning electron microscope, showing a surface of the germanium thin film of the electrode a7 in its state before charge and discharge, when observed from above. Figures 36 is a photomicrograph (secondary electron images) taken with a scanning electron microscope, showing a surface of the germanium thin film of the electrode a8 in its state before charge and discharge, when observed from above. Figures 35 and 36 are both taken at a magnification of 1,000X.

[0124] As shown in Figures 35 and 36, the germanium thin film has irregularities on its surface that follow the profile of those defined on the underlying electrolytic copper foil. The valleys of the germanium thin film are connected to each other like a network. It is understood that the gaps extend along the depth of such valleys to define columnar portions in the germanium thin film.

(SIMS Analysis of Concentration Profile Along Depth)

[0125] Figure 37 is a graphical representation illustrating concentration profiles of constituent elements in the electrode a7 along its depth before it is incorporated in a battery, i.e., before charge and discharge. Figure 38 is a graphical representation illustrating concentration profiles of constituent elements in the electrode a8 along its depth before charge and discharge. The concentration profiles of constituent elements were obtained by a secondary ion mass spectrometry (SIMS) wherein copper ( $^{63}\text{Cu}^+$ ) and germanium ( $^{73}\text{Ge}^+$ ) concentrations were measured along the depth from a surface of the thin film using  $\text{O}_2^+$  as a sputtering source. The abscissa indicates a depth ( $\mu\text{m}$ ) from a surface of the germanium thin film and the ordinate indicates an intensity (count) of each constituent element.

[0126] As can be clearly seen from Figures 37 and 38, copper (Cu), as a current collector constituent, diffuses into the germanium thin film in the vicinity of the current collector and shows a lower concentration at a location closer to the surface of the germanium thin film.

[0127] As discussed above, the germanium thin film contains a current collector constituent, copper, diffused therein, has a higher copper concentration in the vicinity of the current collector, and has a concentration gradient such that a copper concentration becomes lower at a location closer to its surface. Hence, the germanium thin film in the vicinity of the current collector contains a higher concentration of copper unreactive with lithium and a lower concentration of germanium reactive with lithium. In the vicinity of the current collector, the germanium thin film is thus believed to store and release less lithium, undergo less expansion and shrinkage, and produce a lower level of stress. This probably results in the reduced formation of gaps (spaces) which may cause separation or removal of the germanium thin film from the current collector, so that the bottoms of the columnar portions of the germanium thin film can be kept adhered to the current collector.

[0128] As stated above, the germanium thin film in conditions of being divided in columns maintains strong adhesion to the current collector even during charge-discharge cycling. Also, the gaps formed in a fashion to surround the columnar portions serve to relax the stress caused by expansion and shrinkage during charge-discharge cycles. The excellent charge-discharge cycle characteristics are thus obtained.

(EXPERIMENT 5)

(Fabrication of Electrode a9)

[0129] An electrolytic copper foil (18  $\mu\text{m}$  thick) was used for a current collector as a substrate. A silicon thin film was formed on this electrolytic copper foil by an RF sputtering technique. The sputtering was effected at a sputtering gas (Ar) flow rate of 100 sccm, an ambient substrate temperature (not heated), a reaction pressure of 0.1 Pa ( $1.0 \times 10^{-3}$  Torr) and a 200 W RF power. The silicon thin film was deposited to a thickness of about 2  $\mu\text{m}$ .

[0130] The resulting silicon thin film was analyzed by Raman spectroscopy which detected the presence of a peak around  $480 \text{ cm}^{-1}$  and the absence of a peak around  $520 \text{ cm}^{-1}$ . This reveals an amorphous nature of the silicon thin film.

[0131] The electrolytic copper foil after silicon thin film deposition thereon was cut into a 2 cm x 2 cm size to prepare an electrode a9.

[0132] The surface roughness Ra and the mean spacing S of the electrolytic copper foil used were measured using a stylus profiler Dektak<sup>3</sup>ST (available from ULVAC Inc.) with a scanning distance of 2.0 mm. The surface roughness Ra and the mean spacing S were determined to be 0.188  $\mu\text{m}$  and 11  $\mu\text{m}$ , respectively.

(Fabrication of Electrode a10)

[0133] An electrolytic copper foil similar to that used in the fabrication of the electrode a9 was used for a current collector as a substrate. A silicon thin film was formed on the electrolytic copper foil under the same conditions as used in the fabrication of the electrode a1 of Experiment 1 to a thickness of about 2  $\mu\text{m}$ . The procedure used to prepare the electrode a9 was followed to prepare an electrode a10.

[0134] The resulting silicon thin film was analyzed by Raman spectroscopy which detected the presence of peaks around  $480\text{ cm}^{-1}$  and  $520\text{ cm}^{-1}$ . This reveals a microcrystalline nature of the silicon thin film.

(Fabrication of Comparative Electrode b3)

[0135] A rolled copper foil for use in the above Experiment 1 was utilized for a current collector as a substrate. The procedure used to fabricate the electrode a9 was followed to form an amorphous silicon thin film (about  $2\text{ }\mu\text{m}$  thick) on the rolled copper foil by an RF sputtering technique.

[0136] The resulting amorphous silicon thin film was subjected to one-hour annealing at  $650\text{ }^{\circ}\text{C}$ . The annealed silicon thin film was then analyzed by Raman spectroscopy which revealed disappearance of a peak around  $480\text{ cm}^{-1}$  and detected a sole peak around  $520\text{ cm}^{-1}$ . This demonstrates that the annealing results in the formation of a polycrystalline silicon thin film.

[0137] The procedure used to prepare the electrode a9 was followed to prepare an electrode b3 from the polycrystalline silicon thin film formed on the rolled copper foil.

[0138] The above-described procedure was utilized to measure the surface roughness Ra and the mean spacing S for the rolled copper foil. The rolled copper foil exhibited the surface roughness Ra of  $0.037\text{ }\mu\text{m}$  and the mean spacing S of  $14\text{ }\mu\text{m}$ .

(Measurement of Charge-Discharge Characteristics)

[0139] Each of the above-fabricated electrodes a9, a10 and b3 was used as a work electrode. Metallic lithium was used for both a counter electrode and a reference electrode. Using these electrodes, experimental cells were constructed. The electrolyte solution was identical to that used in the above Experiment 1. In a single electrode cell, reduction of the work electrode is a charge reaction and oxidation thereof is a discharge reaction.

[0140] Each experimental cell was charged at a constant current of  $0.5\text{ mA}$  at  $25\text{ }^{\circ}\text{C}$  until a potential relative to the reference electrode reached  $0\text{ V}$ , and then discharged to  $2\text{ V}$ . This was recorded as a unit charge-discharge cycle. Cycling was effected to measure 1st- and 5th-cycle discharge capacities and charge-discharge efficiencies. The results are given in Table 6.

Table 6

			Electrode a9	Electrode a10	Electrode b3
Substrate			Electrolytic Copper Foil	Electrolytic Copper Foil	Rolled Copper Foil
Thickness of Silicon Thin Film			$2\text{ }\mu\text{m}$	$2\text{ }\mu\text{m}$	$2\text{ }\mu\text{m}$
Annealing			Absent	Absent	$650^{\circ}\text{C}$ , 1h
Crystallinity of Silicon Thin Film			Amorphous	Microcrystalline	Polycrystalline
Charge-Discharge Characteristics	1st Cycle	Discharge Capacity (mAh/g)	3980	4020	1978
		Charge-Discharge Efficiency(%)	100	96	83
	5th Cycle	Discharge Capacity (mAh/g)	3990	4020	731
		Charge-Discharge Efficiency(%)	100	100	75

[0141] As apparent from the results shown in Table 6, the electrode a9 using the amorphous silicon thin film for the electrode active material and the electrode a10 using the microcrystalline silicon thin film for the electrode active material, in accordance with the present invention, exhibit higher discharge capacities and superior charge-discharge efficiencies even on the 5th cycle, relative to the comparative electrode b3.

(EXPERIMENT 6)

(EXAMPLES 1 - 7 AND COMPARATIVE EXAMPLES 1 - 2)

(Fabrication of Current Collector)

**[0142]** Samples 1 - 4 specified in Table 7 were used for a current collector as a substrate. Sample 1 was similar to the rolled copper foil used for the current collector of the electrode b3. Samples 2 - 4 were prepared in accordance with the following procedure: A rolled copper foil was ground with a #100, #400 or #1000 emery paper to roughen its surface, washed with a purified water and then dried.

Table 7

Sample No.	1	2	3	4
Copper Foil Thickness ( $\mu\text{m}$ )	18	18	18	18
Surface Roughness Ra ( $\mu\text{m}$ )	0.037	0.1	0.18	1

**[0143]** Each of the above copper foils was used as a substrate. A silicon thin film was deposited on the substrate under the conditions specified in Tables 8 - 10 by means of an RF argon sputtering apparatus. In Comparative Example 2, the deposited thin film was subsequently subjected to a heat treatment (annealing). In Examples 1 - 7 and Comparative Example 1, each substrate was pretreated prior to thin film deposition. The pretreatment was performed by generating an ECR plasma in a separately-installed plasma generator and directing the plasma to bombard the substrate for 10 minutes at a 200 W microwave power and an argon gas partial pressure of 0.06 Pa.

**[0144]** The nature of each silicon thin film was identified via analysis by Raman spectroscopy. The results are shown in Tables 8 - 10.

(Measurement of Charge-Discharge Characteristics)

**[0145]** The silicon-deposited copper foils obtained in Examples 1 - 7 and Comparative Examples 1 - 2 were cut into 2 cm x 2 cm pieces and then utilized to construct experimental cells in the same manner as in the above Experiment 5. For each cell, the charge-discharge test was performed in the same manner as in the above Experiment 5 to measure 1st-, 5th- and 20th-cycle discharge capacities and charge-discharge efficiencies. The results are shown in Tables 8 - 10.

Table 8

	Ex.1	Ex.2	Ex.3	Ex.4
Substrate type	Sample 2	Sample 3	Sample 4	Sample 3
Surface Roughness Ra	0.1	0.18	1	0.18
Substrate Thickness	18 $\mu$ m	18 $\mu$ m	18 $\mu$ m	18 $\mu$ m
Thickness of Silicon Thin Film	2 $\mu$ m	2 $\mu$ m	2 $\mu$ m	2 $\mu$ m
Film-Forming Process	Sputtering	Sputtering	Sputtering	Sputtering
Sputtering Gas	Argon	Argon	Argon	Argon
Ar Flow Rate	100sccm	100sccm	100sccm	100sccm
Target	99.999% Si Single Crystal	99.999% Si Single Crystal	99.999% Si Single Crystal	99.999% Si Single Crystal
Sputtering Atmosphere	0.10Pa	0.10Pa	0.10Pa	0.10Pa
Sputtering Power	200W	200W	200W	200W
Substrate Temperature	20°C	20°C	20°C	200°C
Pretreatment	Present	Present	Present	Present
Sputtering Time	2h	2h	2h	2h
Heat Treatment	Absent	Absent	Absent	Absent
Heat Treating Time	-	-	-	-
Raman Peak at 480cm <sup>-1</sup>	Present	Present	Present	Present
Raman Peak at 520cm <sup>-1</sup>	Absent	Absent	Absent	Absent
Crystallinity	Amorphous	Amorphous	Amorphous	Amorphous
Discharge Capacity(mAh/g)	3980	3978	3975	3980
Charge-Discharge Efficiency(%)	100	100	100	100
Discharge Capacity(mAh/g)	3990	3981	3980	3990
Charge-Discharge Efficiency(%)	100	100	100	100
Discharge Capacity(mAh/g)	3990	3980	3981	3990
Charge-Discharge Efficiency(%)	100	100	100	100

Table 9

		Ex.5	Ex.6	Ex.7
5	Substrate	Substrate type	Sample 3	Sample 3
		Surface Roughness Ra	0.18	0.18
10		Substrate Thickness	18 $\mu$ m	18 $\mu$ m
	Thin Film Forming Conditions	Thickness of Silicon Thin Film	2 $\mu$ m	2 $\mu$ m
15		Film-Forming Process	Sputtering	Sputtering
		Sputtering Gas	Argon	Argon
		Ar Flow Rate	100sccm	100sccm
20		Target	99.999% Si Single Crystal	99.999% Si Single Crystal
		Sputtering Atmosphere	0.10Pa	1.0Pa
25		Sputtering Power	200W	200W
		Substrate Temperature	50°C	20°C
		Pretreatment	Present	Present
30		Sputtering Time	2h	1.5h
	Heat Treatment Conditions	Heat Treatment	Absent	Absent
		Heat Treating Time	-	-
35	Identification of Crystallinity	Raman Peak at 480cm <sup>-1</sup>	Present	Present
		Raman Peak at 520cm <sup>-1</sup>	Absent	Absent
		Crystallinity	Amorphous	Amorphous
40	1st Cycle	Discharge Capacity(mAh/g)	4060	3585
		Charge-Discharge Efficiency (%)	100	100
45	5th cycle	Discharge Capacity(mAh/g)	4060	3592
		Charge-Discharge Efficiency(%)	100	100
50	20th cycle	Discharge Capacity(mAh/g)	4060	3590
		Charge-Discharge Efficiency(%)	100	100

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TABLE 10

		Comp.Ex.1	Comp.Ex.2
5	Substrate	Substrate type	Sample 3
		Surface Roughness Ra	0.18
		Substrate Thickness	18 $\mu$ m
10	Thin Film Forming Conditions	Thickness of Silicon Thin Film	2 $\mu$ m
		Film-Forming Process	Sputtering
		Sputtering Gas	Argon
		Ar Flow Rate	100sccm
		Target	99.999% Si Single Crystal
		Sputtering Atmosphere	0.10Pa
		Sputtering Power	200W
		Substrate Temperature	450°C
		Pretreatment	Present
		Sputtering Time	2h
25	Heat Treatment Conditions	Heat Treatment	Absent
		Heat Treating Time	1h
30	Identification of Crystallinity	Raman Peak at 480cm <sup>-1</sup>	Absent
		Raman Peak at 520cm <sup>-1</sup>	Present
		Crystallinity	Polycrystalline
35	1st Cycle	Discharge Capacity(mAh/g)	1250
		Charge-Discharge Efficiency(%)	81
40	5th cycle	Discharge Capacity(mAh/g)	900
		Charge-Discharge Efficiency(%)	75
45	20th cycle	Discharge Capacity(mAh/g)	700
		Charge-Discharge Efficiency(%)	69

[0146] As can be clearly seen from the results shown in Tables 8 - 10, the increased discharge capacities and improved charge-discharge cycle characteristics are obtained by utilizing the electrodes obtained via Examples 1 - 7 that use the amorphous silicon thin film for the electrode active material in accordance with the present invention, relative to utilizing the electrodes obtained via Comparative Examples 1 - 2 that use the polycrystalline silicon thin film for the electrode active material.

#### (EXPERIMENT 7)

[0147] An amorphous silicon thin film (about 3  $\mu$ m thick) was formed on an electrolytic copper foil (18  $\mu$ m thick, surface roughness Ra = 0.188  $\mu$ m, mean spacing S = 6  $\mu$ m) by an RF sputtering technique to fabricate an electrode a-11. The thin film was deposited using single-crystal silicon as a target, at a sputtering gas (Ar) flow rate of 100 sccm, an ambient substrate temperature (not heated), a reaction pressure of 0.1 Pa, and 200 W RF power.

[0148] The resulting silicon thin film was analyzed by Raman spectroscopy which detected the presence of a peak around  $480\text{ cm}^{-1}$  and the absence of a peak around  $520\text{ cm}^{-1}$ . This revealed an amorphous nature of the silicon thin film.

[0149] The electrode a-11 thus obtained was used to construct a battery A11 in the same manner as in the above Experiment 1. The battery was subjected to a charge-discharge cycle test under the same conditions as in the above Experiment 1 to measure a capacity retention rate on the 30th-cycle. The result is shown in Table 11. In Table 11, the results for the batteries A1 and A3 are also shown.

Table 11

Battery	30th-Cycle Capacity Retention Rate
A1	91%
A3	97%
A11	97%

[0150] As apparent from the results shown in Table 11, the battery A11 using the sputter deposited amorphous silicon thin film for the active material also exhibits a good capacity retention rate comparable to those of the batteries A1 and A3 using the microcrystalline silicon thin film for the active material.

[0151] The condition of the silicon thin film in the electrode a-11 was observed using an electron microscope. First, a section of the electrode a-11 in its state before charge and discharge was observed with a scanning electron microscope. Figures 39 and 40 are photomicrographs (secondary electron images) taken with a scanning electron microscope, each showing a section of the electrode a-11 before charge and discharge. Figures 39 and 40 are taken at magnifications of 2,000X and 10,000X, respectively. A sample was prepared by following the procedure used to prepare the samples shown in Figures 2 and 3, i.e., by embedding the electrode in a resin and then slicing the resin-embedded electrode.

[0152] In Figures 39 and 40, a portion that appears relatively light indicates the electrolytic copper foil. The deposited silicon thin film (about  $3\text{ }\mu\text{m}$  thick) is found as a dark portion on the copper foil. As shown in Figures 39 and 40, irregularities are defined on a surface of the electrolytic copper foil. Particularly, projections have a generally conical shape. Similar irregularities with such conical projections are also formed on a surface of the silicon thin film deposited on the copper foil. Accordingly, the surface irregularities of the silicon thin film appear to conform in shape to those defined on the copper foil surface.

[0153] Figure 41 is a photomicrograph (secondary electron image) taken with a scanning electron microscope, showing a surface of the silicon thin film in the electrode a-11 when viewed at a magnification of 1,000X. As shown in Figure 41, a number of projections is formed on the silicon thin film surface. As shown in Figures 39 and 40, these projections are formed in such a way to follow those defined on the copper foil surface.

[0154] Figure 42 is a photomicrograph (reflection electron image) taken with a scanning electron microscope, showing a surface of the electrode a-11 removed from the battery A11 after 30 cycles in the charge-discharge test. Figure 42 is a photograph taken at a magnification of 1,000X.

[0155] As shown in Figure 42, gaps (spaces) are formed in the silicon thin film to extend in its thickness direction and these gaps (spaces) divide the silicon thin film into columns. In the silicon thin film shown in Figures 6 - 9, the gaps are formed in such a way as to define columnar portions each encompassing a single projection on the thin film. On the other hand, in the silicon thin film shown in Figure 42, the gaps are formed in such a way as to define columnar portions each encompassing plural projections on the thin film. It is also found that the gaps (spaces) are wider in the silicon thin film shown in Figure 42 than in the silicon thin film shown in Figures 6 - 9.

[0156] The battery A11 exhibits a good capacity retention in a manner similar to the battery A3. This is believed to demonstrate that the spaces provided in a way to surround the columnar portions serve to relax the stress caused by expansion and shrinkage of the active material so that charge-discharge cycling can be repeated without occurrence of separation of the active material from the current collector, even in the case where each columnar portion is defined to encompass plural projections on the thin film surface.

#### (EXPERIMENT 8)

[0157] An about  $2\text{ }\mu\text{m}$  thick, microcrystalline silicon thin film was formed on both a rolled copper foil and an electrolytic copper foil ( $18\text{ }\mu\text{m}$  thick) under the same thin film-forming conditions as used in the fabrication of electrode a1 in Experiment 1. Then, a 17 mm diameter piece was punched out from each sample to provide an electrode c1 incorporating the silicon thin film formed on the rolled copper foil and an electrode c3 incorporating the silicon thin film formed on the electrolytic copper foil. Pieces identical to the electrodes c1 and c3 were heat treated at  $400\text{ }^{\circ}\text{C}$  for 3 hours to provide electrodes c2 and c4, respectively.

[0158] The procedure of Experiment 1 was followed, except that the electrodes c1 - c4 were used for the negative electrode, to construct rechargeable lithium batteries C1 - C4. These batteries were measured for charge-discharge cycle life characteristics in the same manner as in Experiment 1. Also, a hydrogen content, a ratio of Raman peak intensities ( $480\text{ cm}^{-1}/520\text{ cm}^{-1}$ ) and a crystal grain size were measured for the silicon thin film of each electrode in the same manner as in Experiment 1. The results are shown in Table 12.

Table 12

Battery	50th-Cycle Capacity Retention Rate	Hydrogen Content	Ratio of Peak Intensities ( $480\text{ cm}^{-1}/520\text{ cm}^{-1}$ ) ( $480\text{ cm}^{-1}/520\text{ cm}^{-1}$ )	Crystal Grain Size
C1	90%	4%	0.1	1nm
C2	85%	0.01%	0.1	1nm
C3	91%	4%	0.1	1nm
C4	87%	0.01%	0.1	1nm

[0159] As demonstrated by the results shown in Table 12, the markedly high capacity retention rates are also obtained for the batteries C1 - C4 with the about  $2\text{ }\mu\text{m}$  thick microcrystalline silicon thin film.

[0160] The electrode c1 incorporating the microcrystalline silicon thin film formed on the rolled copper foil was sliced in its thickness direction to provide a sample which was subsequently observed with a transmission electron microscope.

[0161] Figures 43 and 44 are photomicrographs taken with a transmission electron microscope, showing an interface between the copper foil and the silicon thin film and its vicinities in the electrode c1. Figures 43 and 44 are taken at magnifications of 500,000X and 1,000,000X. The copper foil is found in a lower portion and the silicon thin film in an upper portion of each photomicrograph.

[0162] In Figures 43 and 44, a lightened lower portion appears to be a copper foil portion. A portion located in the vicinity of the interface between the copper foil and silicon thin film appears darkened toward the above. This portion (about  $30\text{ nm}$  - about  $100\text{ nm}$ ) seems to be a part of a mixed layer where diffusion of copper from the copper foil into silicon is particularly significant. In this mixed layer, copper (Cu) is probably alloyed with silicon (Si). Also in Figures 43 and 44, a particulate portion is observed in the vicinity of an interface between the seeming mixed layer and the copper foil. This particulate portion is found to define an irregular profile along the interface as a result of the diffusion of copper (Cu) into silicon (Si).

[0163] Next, concentration profiles of constituent elements along the depth of the mixed layer were observed. For this purpose, the concentrations of copper ( $^{63}\text{Cu}^+$ ) and hydrogen ( $^1\text{H}^+$ ) were measured by SIMS using  $\text{O}_2^+$  as a sputtering source. Figure 45 shows a concentration profile of each constituent element. The abscissa indicates a depth ( $\mu\text{m}$ ) and the ordinate indicates an atomic density (number of atoms/ $\text{cm}^3$ ).

[0164] As shown in Figure 45, the concentration of copper (Cu) in the mixed layer increases at a deeper location, i. e., at a location closer to the copper foil. If the mixed layer is defined as a layer in the silicon thin film that contains at least 1 % ( $10^{20}$  atoms/ $\text{cm}^3$ , if expressed in atomic density) of a current collector material, the mixed layer is found to exist in a thickness region which extends from a depth of about  $1.9\text{ }\mu\text{m}$  to a depth of about  $2.7\text{ }\mu\text{m}$ .

[0165] Similarly, a concentration profile of each constituent element along the depth of the mixed layer were observed using SIMS for the the electrode c3 incorporating the about  $2\text{ }\mu\text{m}$  thick microcrystalline silicon thin film formed on the electrolytic copper foil. The results are shown in Figure 46. As shown in Figure 46, the atomic density of copper already exceeds  $10^{20}$  atoms/ $\text{cm}^3$  at the surface of the silicon thin film in the electrode c3. This clearly indicates that the copper diffused across the the silicon thin film to its surface to render the silicon thin film into the form of mixed layer in its entirety. Also, the battery C3 using this electrode c3 exhibits good charge-discharge cycle characteristics. This demonstrates that the silicon thin film still serves as electrode active material, even if it is rendered into the form of mixed layer in its entirety.

[0166] As can be clearly seen from Figures 45 and 46, the copper concentration varies continuously across the silicon thin film. This accordingly demonstrates that copper exists in the silicon thin film not in the form of an intermetallic compound with silicon but in the form of a solid solution with silicon.

[0167] As discussed above, it is ascertained that the mixed layer where copper in the copper foil is mixed with silicon in the silicon thin film is formed at the interface between the copper foil and silicon thin film. The presence of this mixed layer is believed to improve adhesion of the silicon thin film to the copper foil, prevent separation of the silicon thin film from the copper foil as a substrate even if the silicon thin film is subjected to expansion and shrinkage on charge and discharge, and provide good charge-discharge cycle characteristics.



## UTILITY IN INDUSTRY

[0168] Rechargeable lithium batteries which exhibit high charge-discharge capacities and good charge-discharge cycle characteristics can be obtained with the use of the electrode in accordance with the present invention.

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## Claims

1. An electrode for a lithium battery having a thin film composed of active material capable of lithium storage and release and provided on a current collector;  
 10       said electrode being **characterized in that** said thin film is divided into columns by gaps formed therein in a manner to extend in its thickness direction, and said columnar portions are at their bottoms adhered to said current collector.
- 15   2. The electrode for a lithium battery as recited in claim 1, **characterized in that** at least a half of thickness portion of said thin film is divided into columns by said gaps.
3. The electrode for a lithium battery as recited in claim 1 or 2, **characterized in that** said thin film has on its surface irregularities including projections and valleys, and said gaps are formed such that each of said columnar portions encompasses at least one projection on a surface of the thin film.  
 20
4. The electrode for a lithium battery as recited in claim 3, **characterized in that** said gaps are formed such that each of said columnar portions encompasses plural projections on the thin film surface.
- 25   5. The electrode for a lithium battery as recited in any one of claims 1 - 4, **characterized in that** said gaps are formed during the first or subsequent charge-discharge cycle.
6. The electrode for a lithium battery as recited in claim 5, **characterized in that** said irregularities are formed on a surface of the thin film before being subjected to charge and discharge, said gaps are formed in the thin film during the first or subsequent charge-discharge cycle in a manner to extend from the valleys of the irregularities on the thin film surface, and the thin film is divided by these gaps into columns.  
 30
7. The electrode for a lithium battery as recited in claim 6, **characterized in that** said irregularities on a surface of the thin film are formed to conform in shape to irregularities on a surface of the underlying current collector.  
 35
8. The electrode for a lithium battery as recited in claim 7, **characterized in that** the projections of the irregularities on a surface of said current collector have a substantially conical shape.
9. The electrode for a lithium battery as recited in any one of claims 1 - 8, **characterized in that** said columnar portions have a round top.  
 40
10. The electrode for a lithium battery as recited in any one of claims 1 - 4 and 9, **characterized in that** said gaps are formed in the thin film before it is subjected to charge and discharge.
- 45   11. The electrode for a lithium battery as recited in any one of claims 1 - 10, **characterized in that** said thin film comprises at least one material that can produce compounds or solid solutions with lithium, selected from elements from Groups IIB, IIIB, IVB and VB of the periodic table, and oxides and sulfides of transition metal elements from Periods 4, 5 and 6 of the periodic table.
- 50   12. The electrode for a lithium battery as recited in claim 11, **characterized in that** said element is at least one selected from carbon, silicon, germanium, tin, lead, aluminum, indium, zinc, cadmium, bismuth and mercury.
13. The electrode for a lithium battery as recited in claim 11, **characterized in that** said element is silicon or germanium.
- 55   14. The electrode for a lithium battery as recited in any one of claims 1 - 13, **characterized in that** said thin film is formed by a CVD, sputtering, vapor evaporation, spraying, or plating process.
15. The electrode for a lithium battery as recited in any one of claims 1 - 14, **characterized in that** said thin film is a

noncrystalline thin film.

16. The electrode for a lithium battery as recited in any one of claims 1 - 14, **characterized in that** said thin film is an amorphous thin film.
17. The electrode for a lithium battery as recited in any one of claims 1 - 10, **characterized in that** said thin film is a noncrystalline silicon thin film.
18. The electrode for a lithium battery as recited in any one of claims 1 - 10, **characterized in that** said thin film is a microcrystalline or amorphous silicon thin film.
19. The electrode for a lithium battery as recited in any one of claims 1 - 10, **characterized in that** said thin film is a noncrystalline germanium thin film.
20. The electrode for a lithium battery as recited in any one of claims 1 - 10, **characterized in that** said thin film is a microcrystalline or amorphous germanium thin film.
21. The electrode for a lithium battery as recited in any one of claims 1 - 10, **characterized in that** said thin film is a microcrystalline or amorphous silicon-germanium alloy thin film.
22. The electrode for a lithium battery as recited in any one of claims 1 - 21, **characterized in that** said current collector comprises at least one selected from copper, nickel, stainless steel, molybdenum, tungsten and tantalum.
23. The electrode for a lithium battery as recited in any one of claims 1 - 22, **characterized in that** said current collector has a surface roughness Ra in the range of 0.01 - 1  $\mu\text{m}$ .
24. The electrode for a lithium battery as recited in any one of claims 1 - 23, **characterized in that** said current collector comprises a copper foil.
25. The electrode for a lithium battery as recited in claim 24, **characterized in that** said copper foil is an electrolytic copper foil.
26. The electrode for a lithium battery as recited in any one of claims 1 - 25, **characterized in that** said gaps are formed along low-density regions in the thin film that extend in a thickness direction of the thin film.
27. The electrode for a lithium battery as recited in claim 26, **characterized in that** said low-density regions extend upwardly from valleys of irregularities on a surface of the current collector.
28. The electrode for a lithium battery as recited in any one of claims 1 - 27, **characterized in that** a constituent of said current collector is diffused into said thin film.
29. The electrode for a lithium battery as recited in claim 28, **characterized in that** said diffused current collector constituent forms, in said thin film, a solid solution, instead of an intermetallic compound, with a component of said thin film.
30. The electrode for a lithium battery as recited in any one of claims 1 - 29, **characterized in that** said thin film is an active thin film which stores lithium via formation of an alloy with lithium.
31. The electrode for a lithium battery as recited in any one of claims 1 - 30, **characterized in that** lithium is previously stored or incorporated in the thin film.
32. A lithium battery including a negative electrode comprising the electrode as recited in any one of claims 1 - 31, a positive electrode and an electrolyte.
33. A rechargeable lithium battery including a negative electrode comprising the electrode as recited in any one of claims 1 - 31, a positive electrode and a nonaqueous electrolyte.
34. The rechargeable lithium battery as recited in claim 33, **characterized in that** said positive electrode contains, as

active material, an oxide capable of lithium storage and release.

35. The rechargeable lithium battery as recited in claim 33, **characterized in that** said positive electrode contains, as active material, a lithium-containing oxide.

36. An electrode for a rechargeable battery which includes an electrode material layer in the form of a thin film and a current collector adhered to the electrode material layer,  
said electrode being **characterized in that** said thin film has low-density regions connected to each other like a network in a planar direction and extending in a thickness direction of the thin film toward said current collector.

37. The electrode for a rechargeable battery as recited in claim 36, **characterized in that** a constituent of said current collector is diffused into said thin film.

38. The electrode for a rechargeable battery as recited in claim 37, **characterized in that** said diffused current collector constituent forms, in said thin film, a solid solution, instead of an intermetallic compound, with a component of said thin film.

39. The electrode for a rechargeable battery as recited in any one of claims 36 - 38, **characterized in that** said thin film is formed on said current collector by a thin film-forming method.

40. The electrode for a rechargeable battery as recited in claim 39, **characterized in that** said thin film-forming method is a CVD, sputtering, vapor evaporation, spraying, or plating process.

41. The electrode for a rechargeable battery as recited in any one of claims 36 - 40, **characterized in that** said current collector has irregularities on its surface and said low-density regions are formed in a manner to extend from valleys of the irregularities.

42. The electrode for a rechargeable battery as recited in claim 41, **characterized in that** projections of the irregularities on the current collector surface have a conical shape.

43. The electrode for a rechargeable battery as recited in any one of claims 36 - 42, **characterized in that** said thin film has on its surface irregularities which conform in shape to irregularities on the current collector surface.

44. The electrode for a rechargeable battery as recited in any one of claims 36 - 43, **characterized in that** said thin film is divided into columns by gaps formed in the thickness direction along the low-density regions as a result of expansion and shrinkage of the thin film.

45. The electrode for a rechargeable battery as recited in claim 44, **characterized in that** the expansion and shrinkage of said thin film are caused to occur by charge and discharge.

46. The electrode for a rechargeable battery as recited in any one of claims 36 - 45, **characterized in that** said thin film is a silicon thin film.

47. The electrode for a rechargeable battery as recited in claim 46, **characterized in that** said silicon thin film is an amorphous or microcrystalline silicon thin film.

48. The electrode for a rechargeable battery as recited in any one of claims 36 - 45, **characterized in that** said thin film is a germanium thin film.

49. The electrode for a rechargeable battery as recited in claim 48, **characterized in that** said germanium thin film is an amorphous or microcrystalline germanium thin film.

50. The electrode for a rechargeable battery as recited in any one of claims 36 - 45, **characterized in that** said thin film is a silicon-germanium alloy thin film.

51. The electrode for a rechargeable battery as recited in claim 50, **characterized in that** said silicon-germanium alloy thin film is an amorphous or microcrystalline silicon-germanium alloy thin film.

52. The electrode for a rechargeable battery as recited in any one of claims 36 - 51, **characterized in that** said current collector has a surface roughness Ra in the range of 0.01 - 1  $\mu\text{m}$ .

5 53. The electrode for a rechargeable battery as recited in any one of claims 36 - 52, **characterized in that** said current collector comprises a copper foil.

54. The electrode for a rechargeable battery as recited in claim 53, **characterized in that** said copper foil is an electrolytic copper foil.

10 55. A rechargeable battery **characterized** as utilizing the electrode as recited in any one of claims 36 - 54.

56. The rechargeable battery as recited in claim 55, **characterized in that** said electrode is used for the positive and/or negative electrode of the rechargeable battery.

15 57. The rechargeable battery as recited in claim 54 or 56, **characterized in that** said rechargeable battery is a non-aqueous rechargeable battery.

20 58. The rechargeable battery as recited in claim 57, **characterized in that** said nonaqueous rechargeable battery is a rechargeable lithium battery.

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FIG. 1

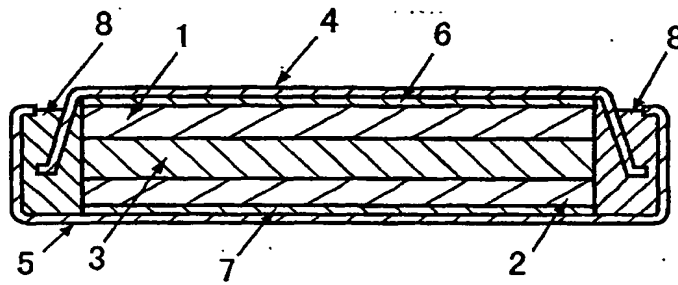


FIG. 2

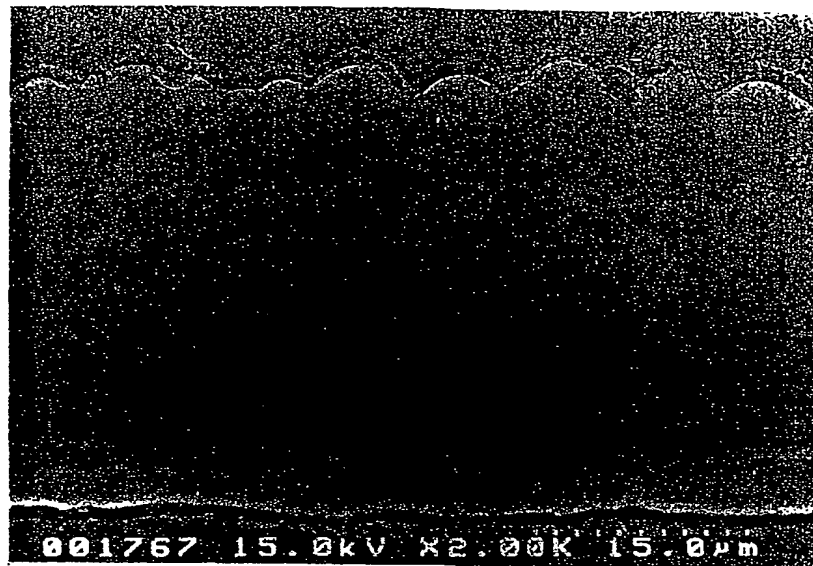


FIG. 3



FIG. 4

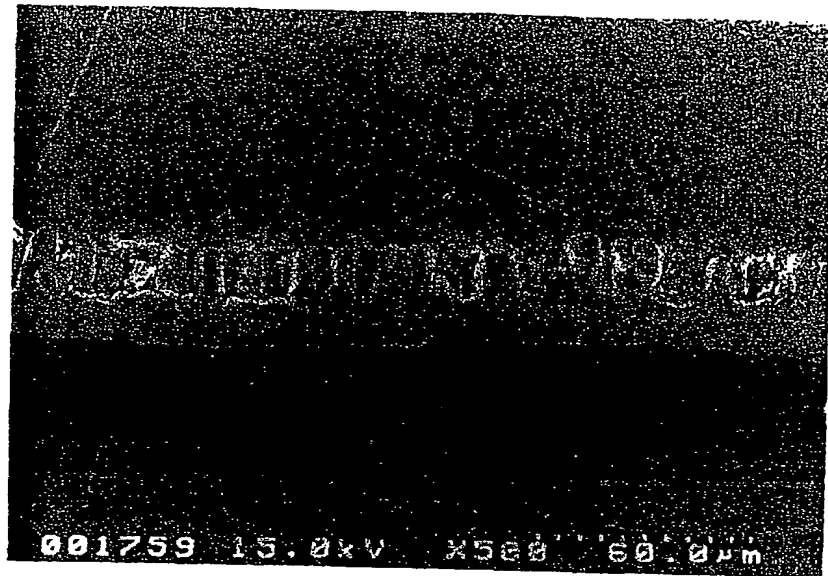


FIG. 5

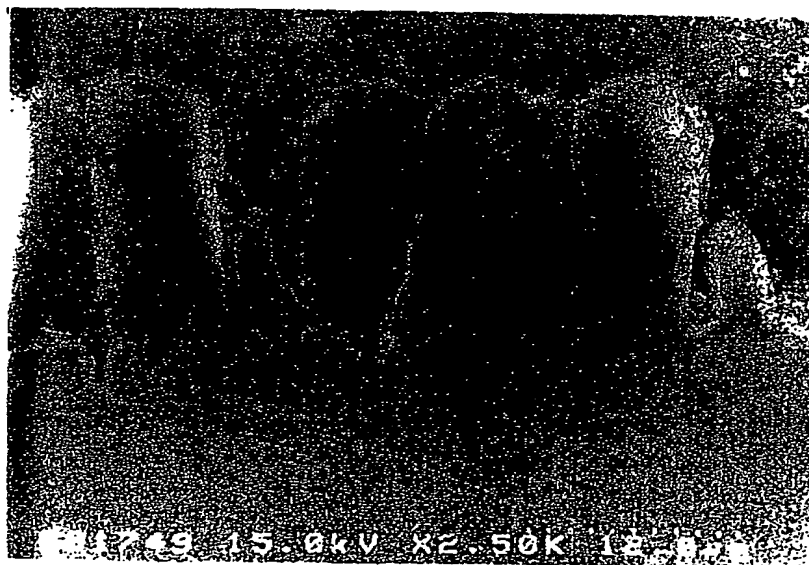


FIG. 6

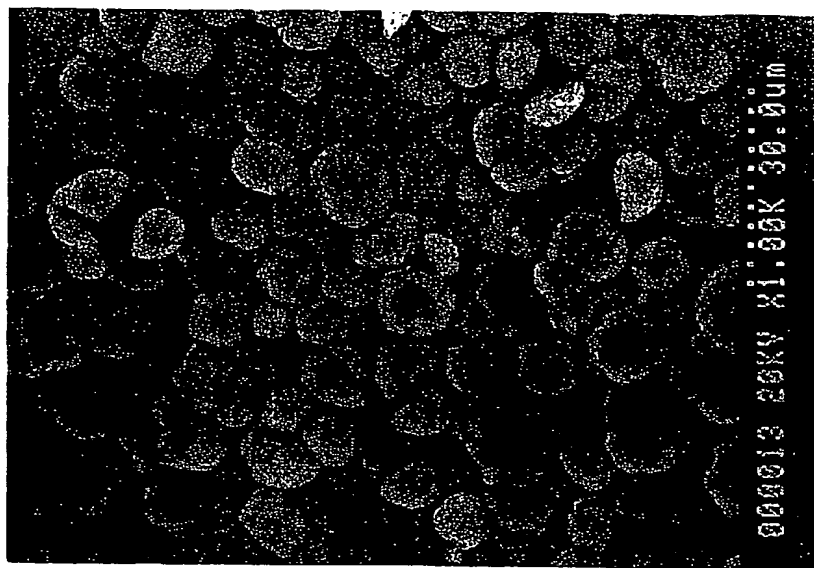


FIG. 7

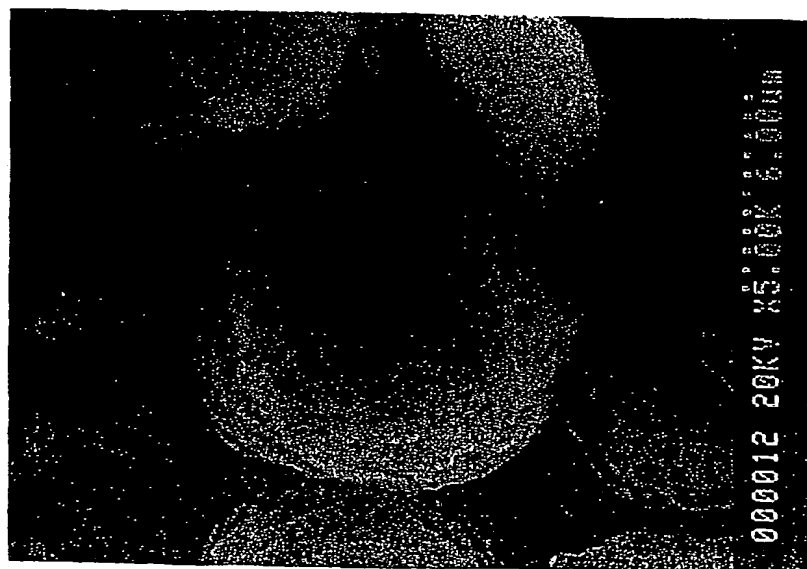




FIG. 8

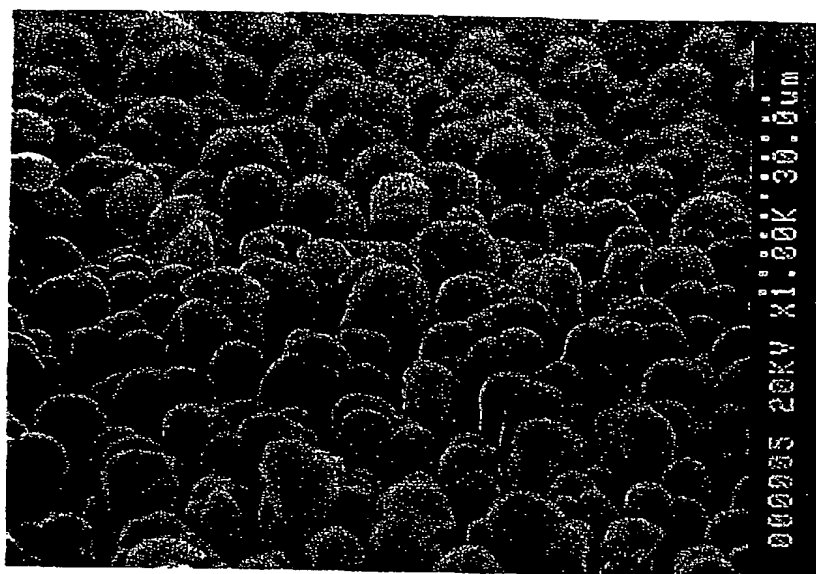


FIG. 9



FIG. 10

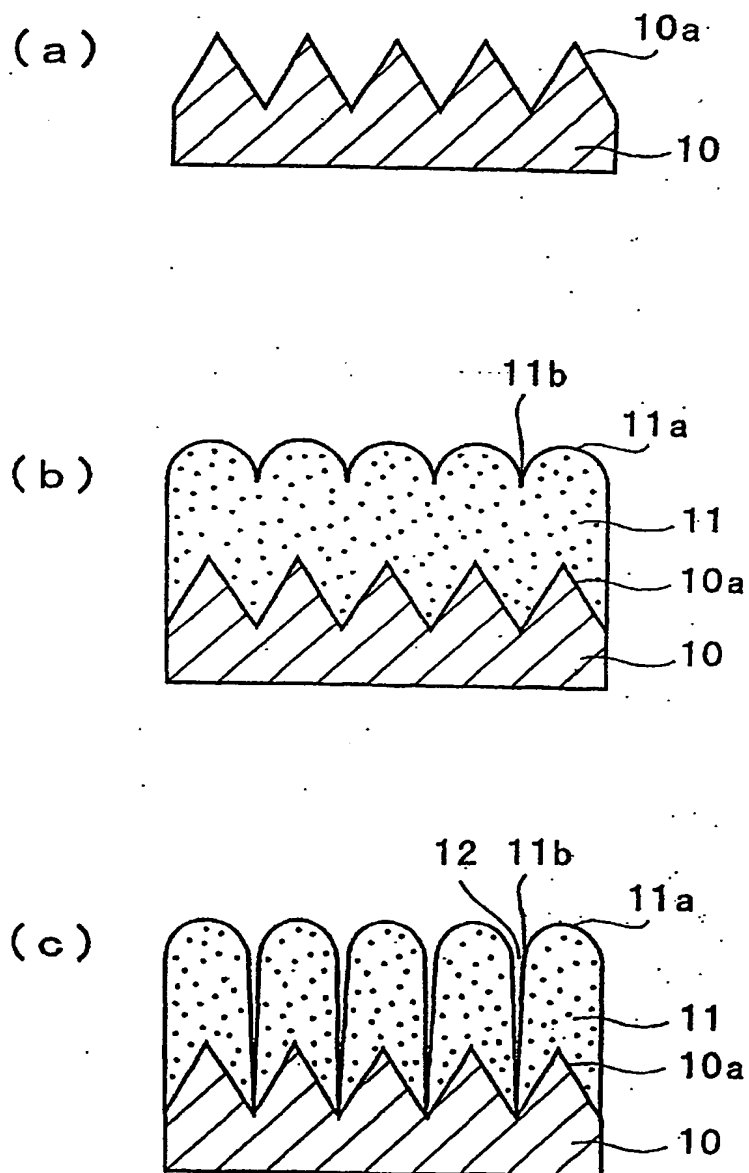


FIG. 11

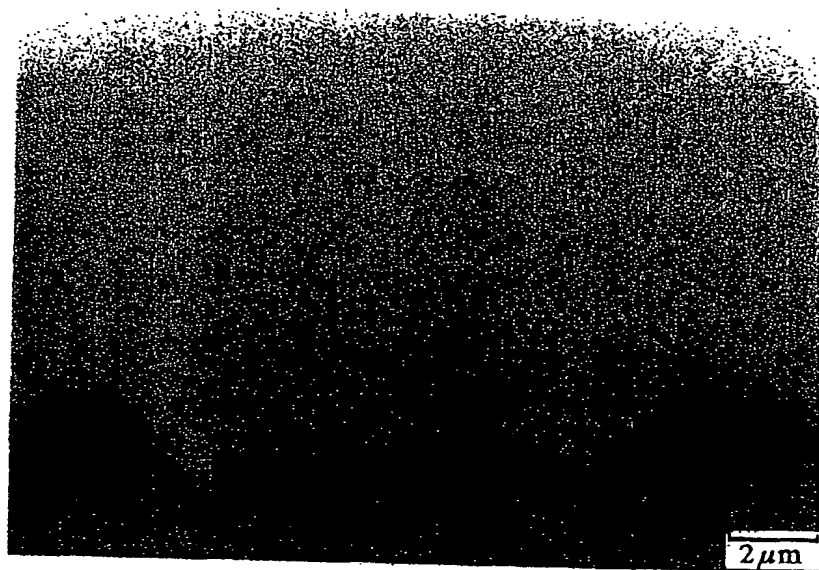


FIG. 12

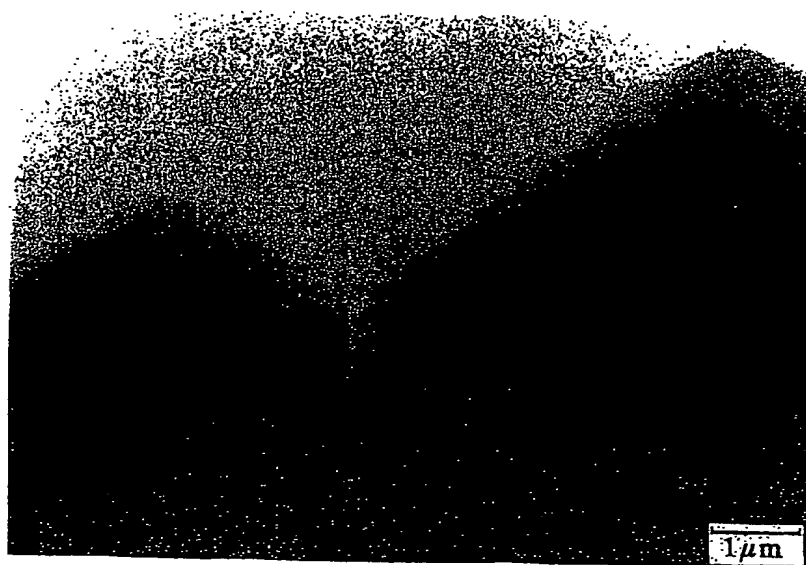


FIG. 13

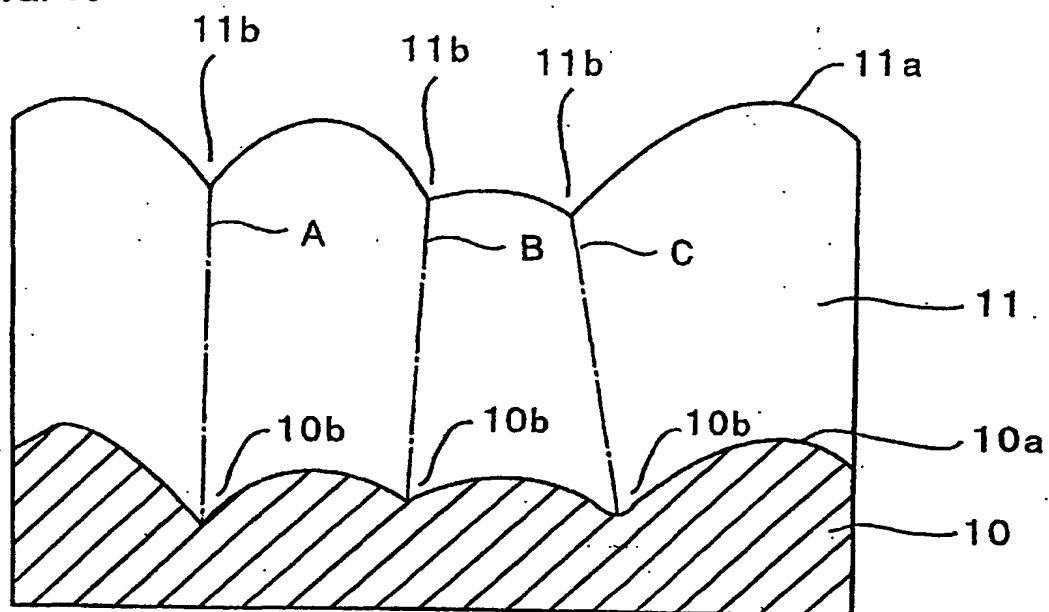


FIG. 14

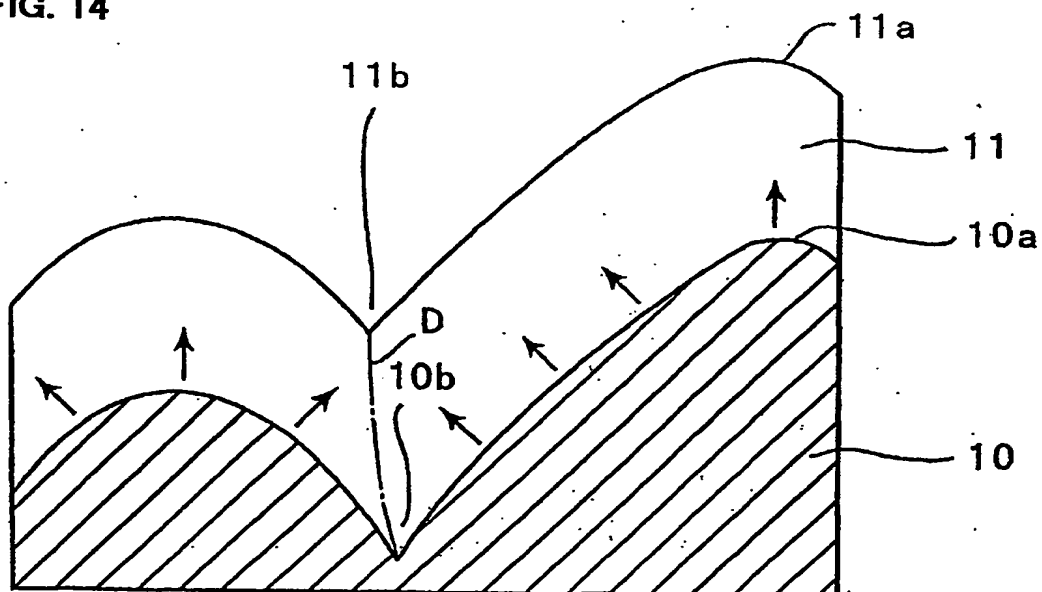


FIG. 15

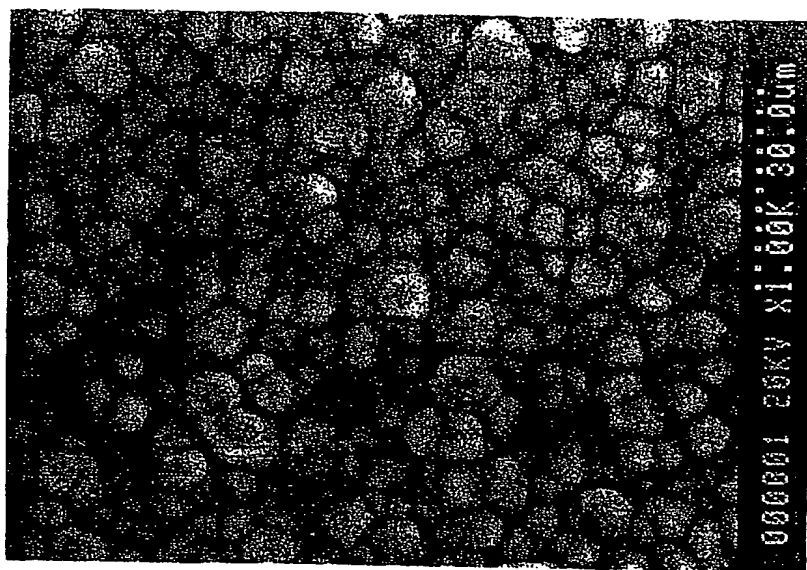


FIG. 16

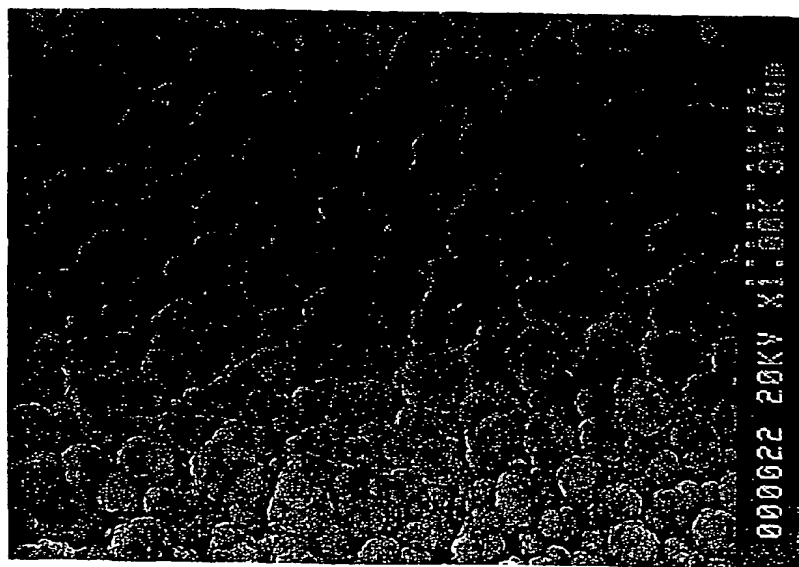


FIG. 17

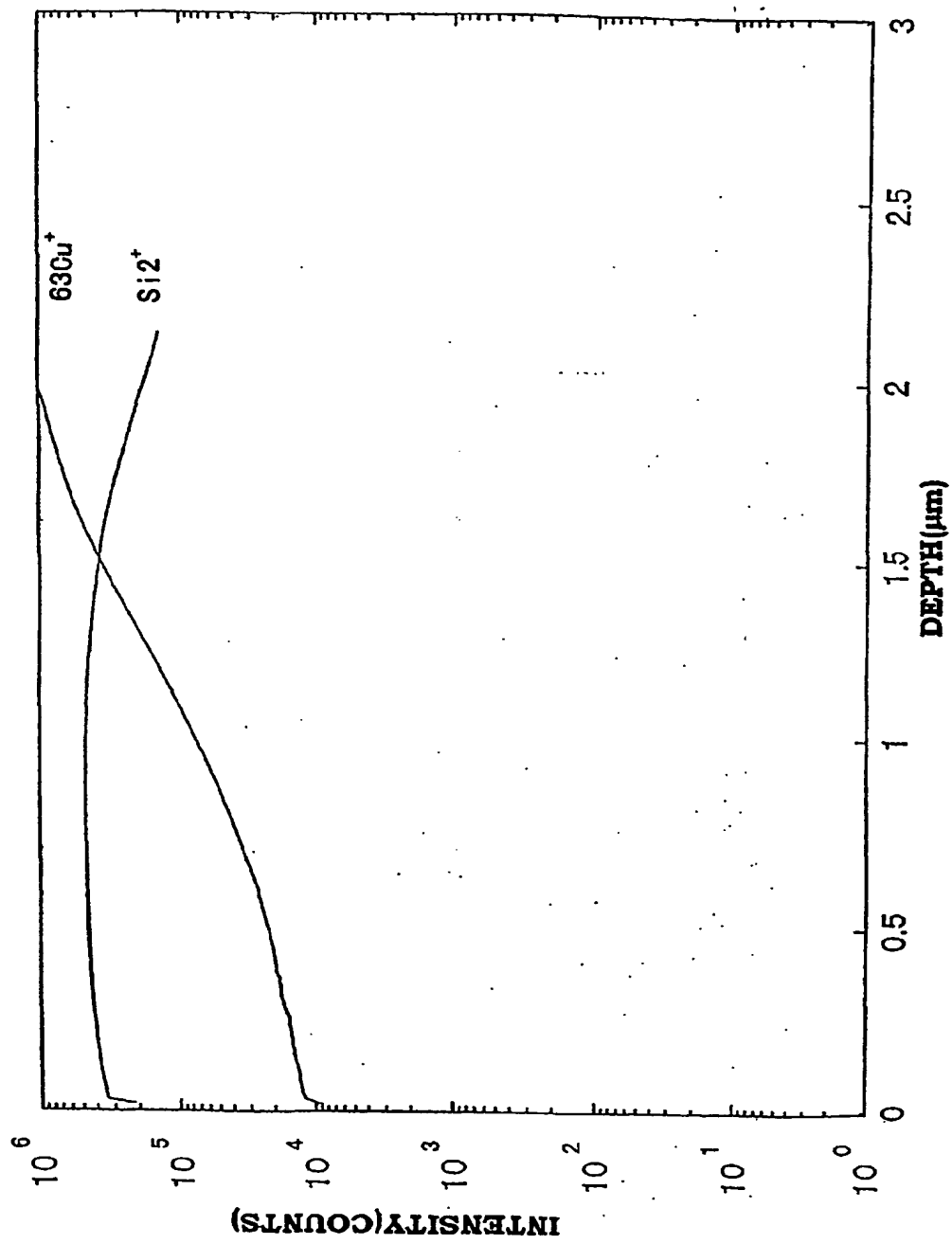


FIG. 18

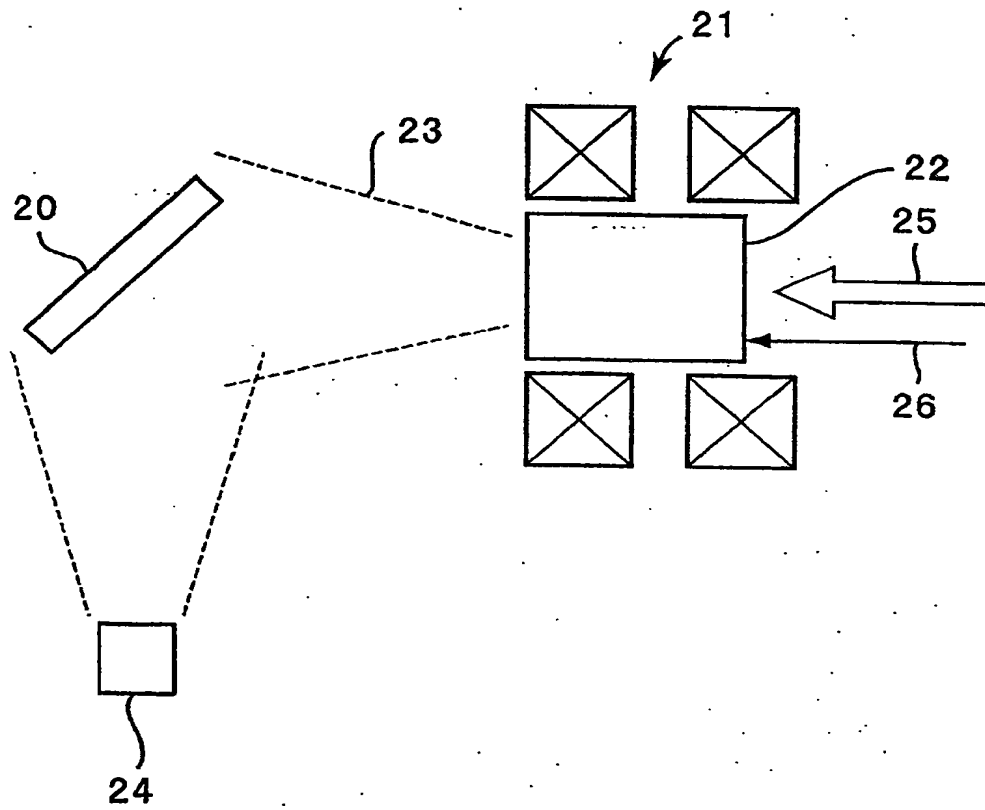


FIG. 19

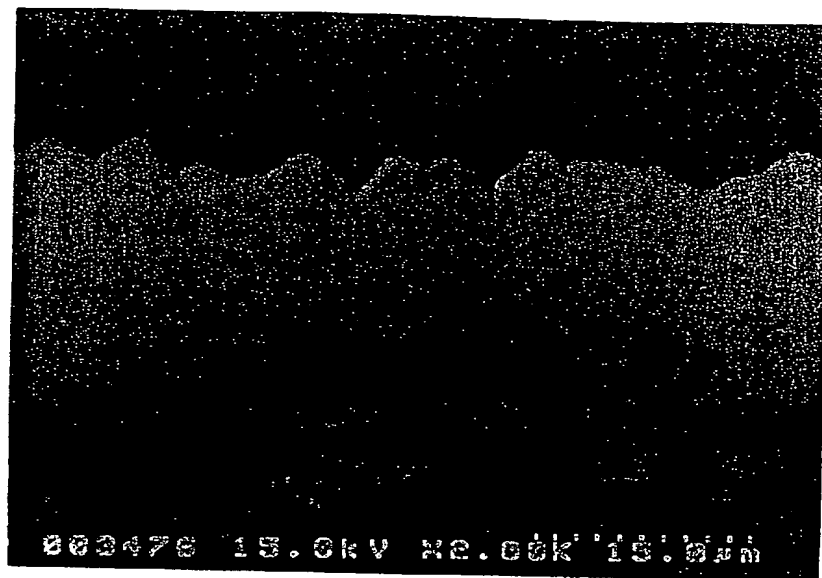


FIG. 20

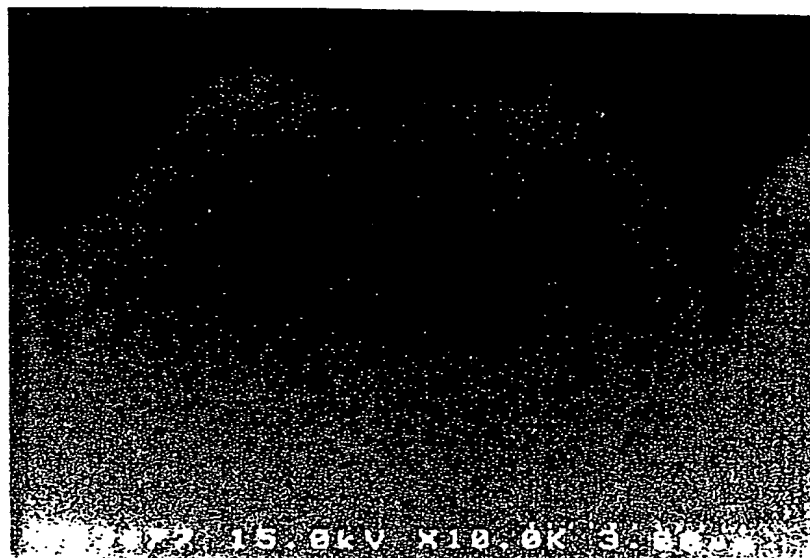




FIG. 21

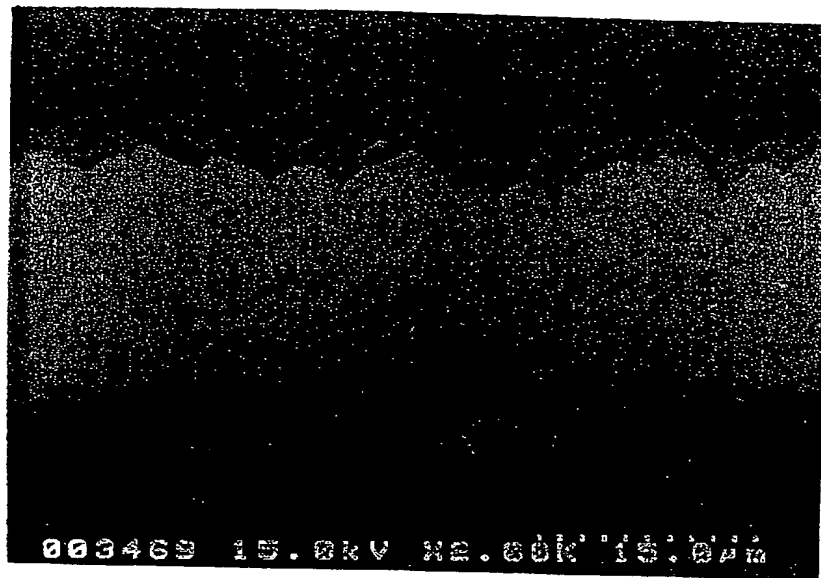


FIG. 22

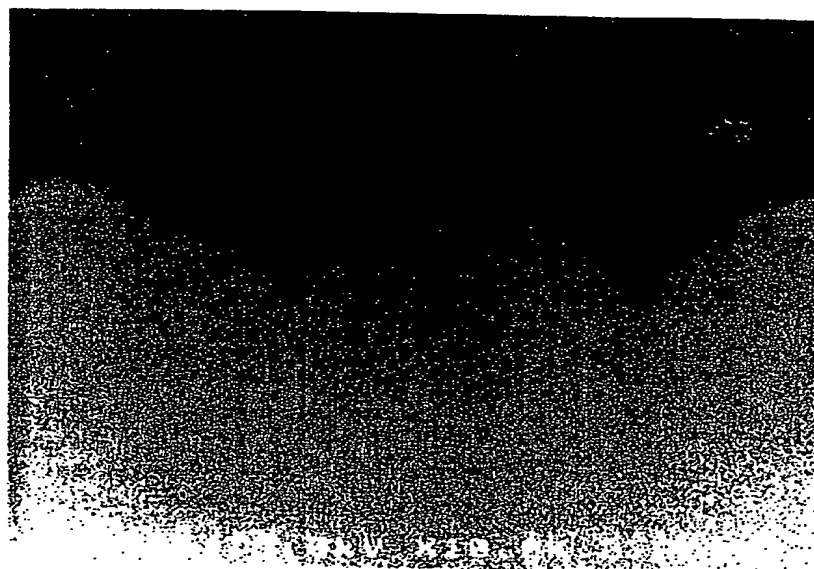


FIG. 23

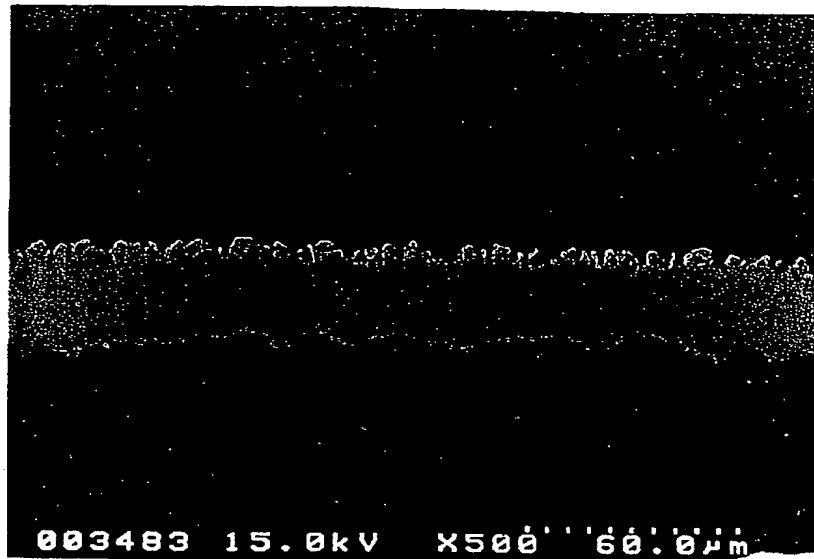


FIG. 24

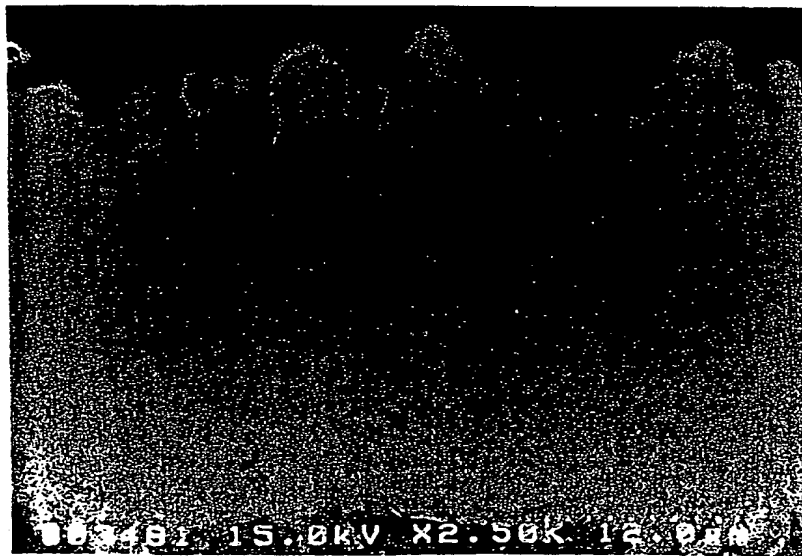


FIG. 25

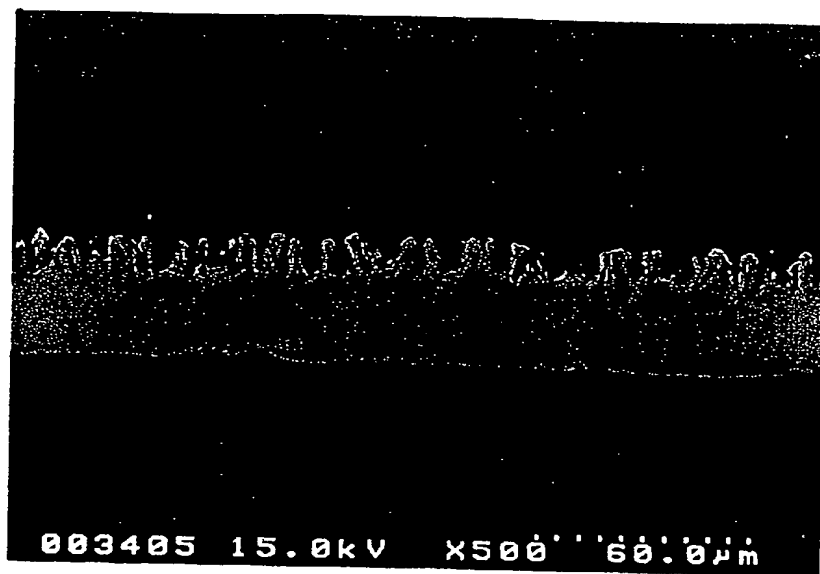


FIG. 26



FIG. 27

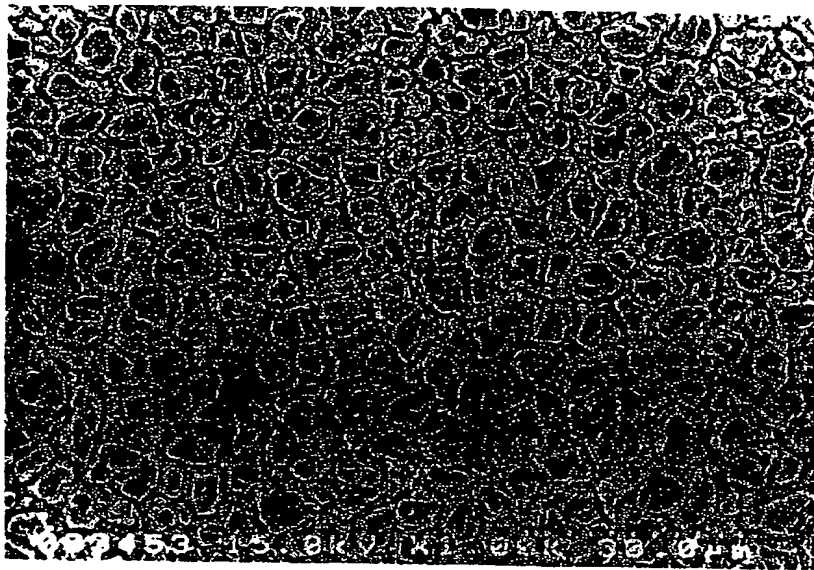


FIG. 28



FIG. 29

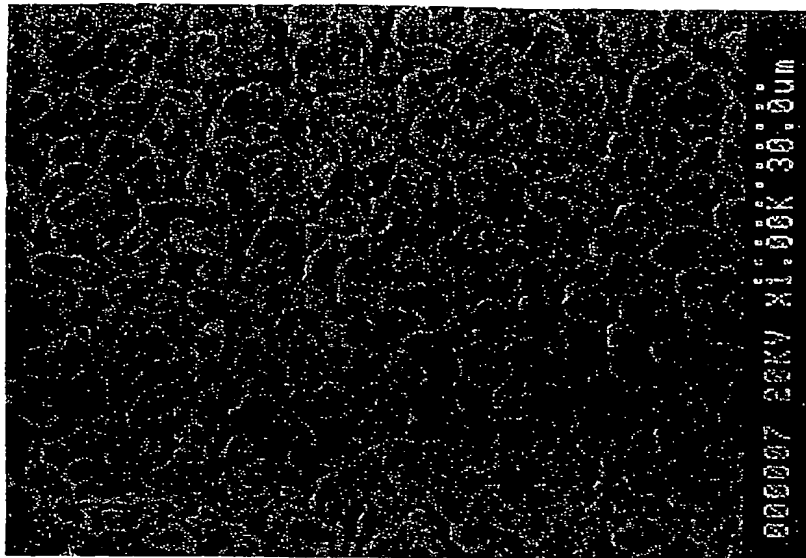


FIG. 30



FIG. 31

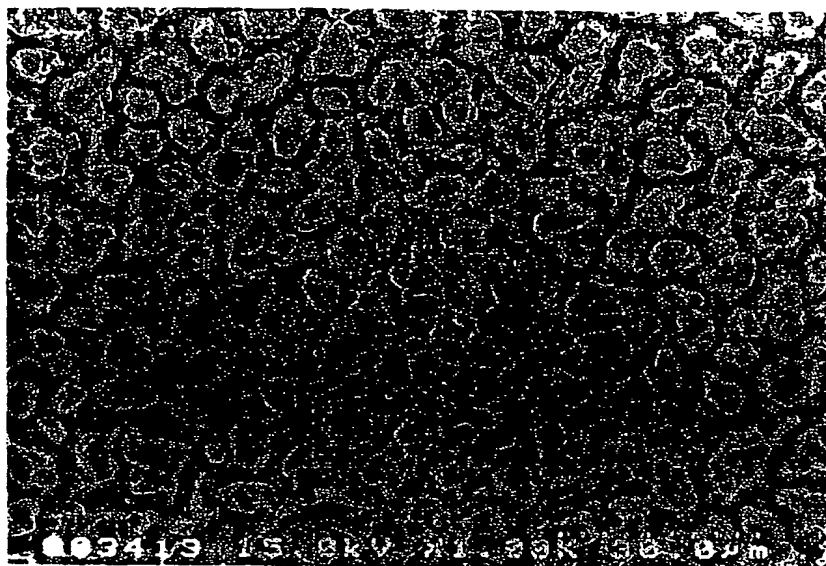
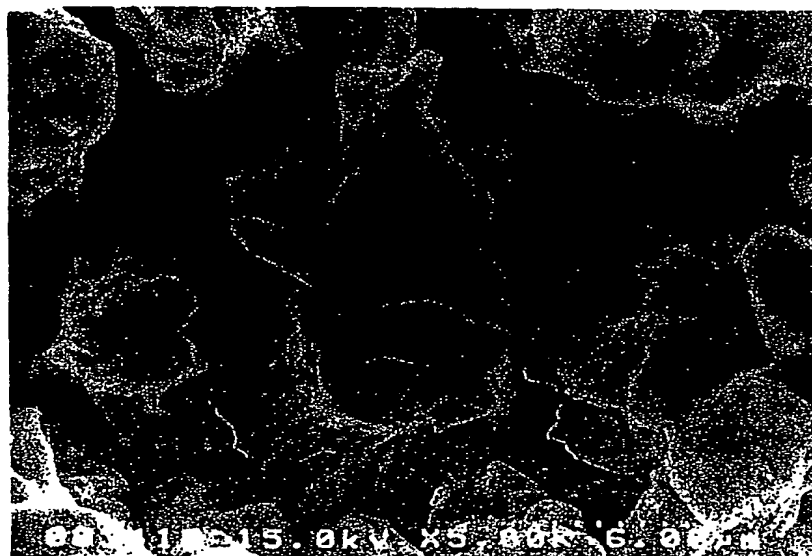
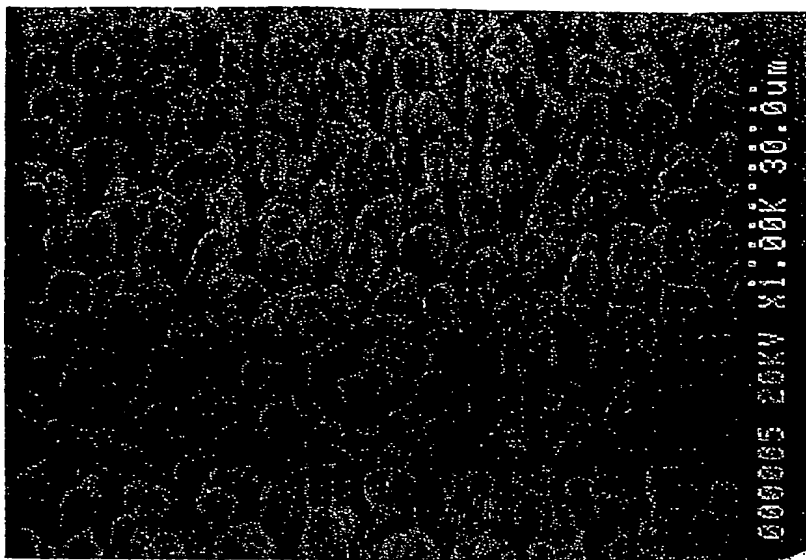


FIG. 32



**FIG. 33**



**FIG. 34**



FIG. 35

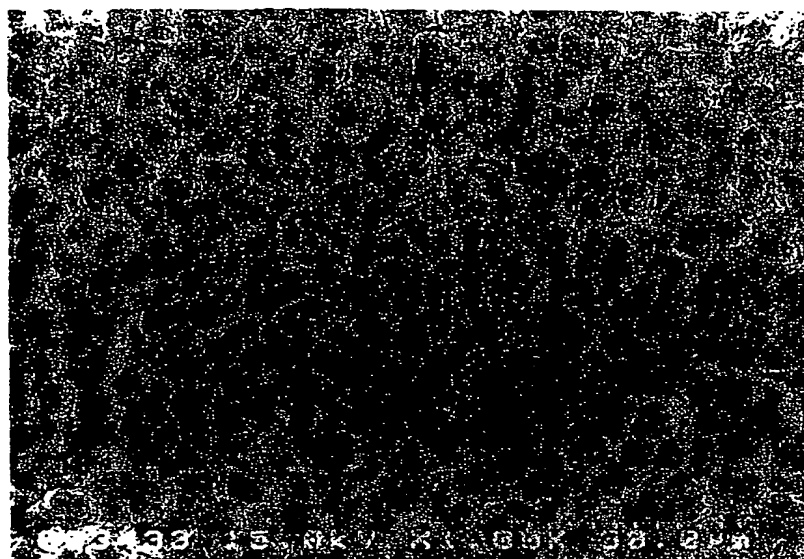


FIG. 36

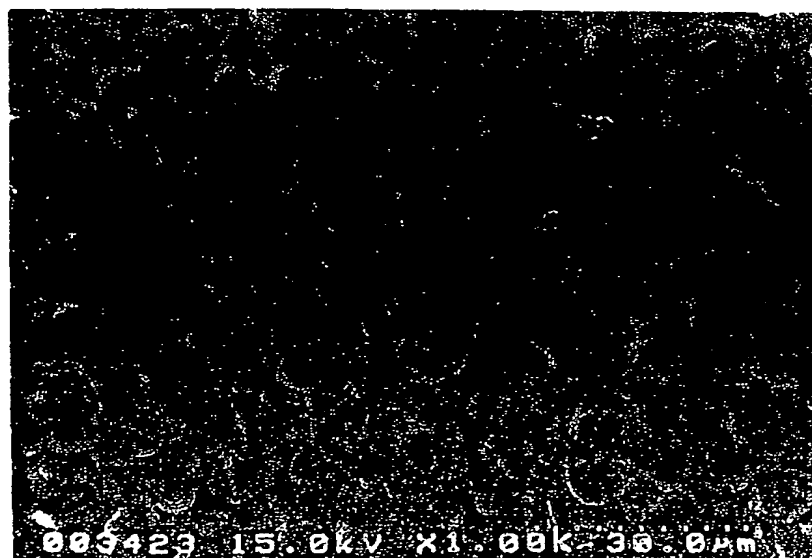




FIG. 37

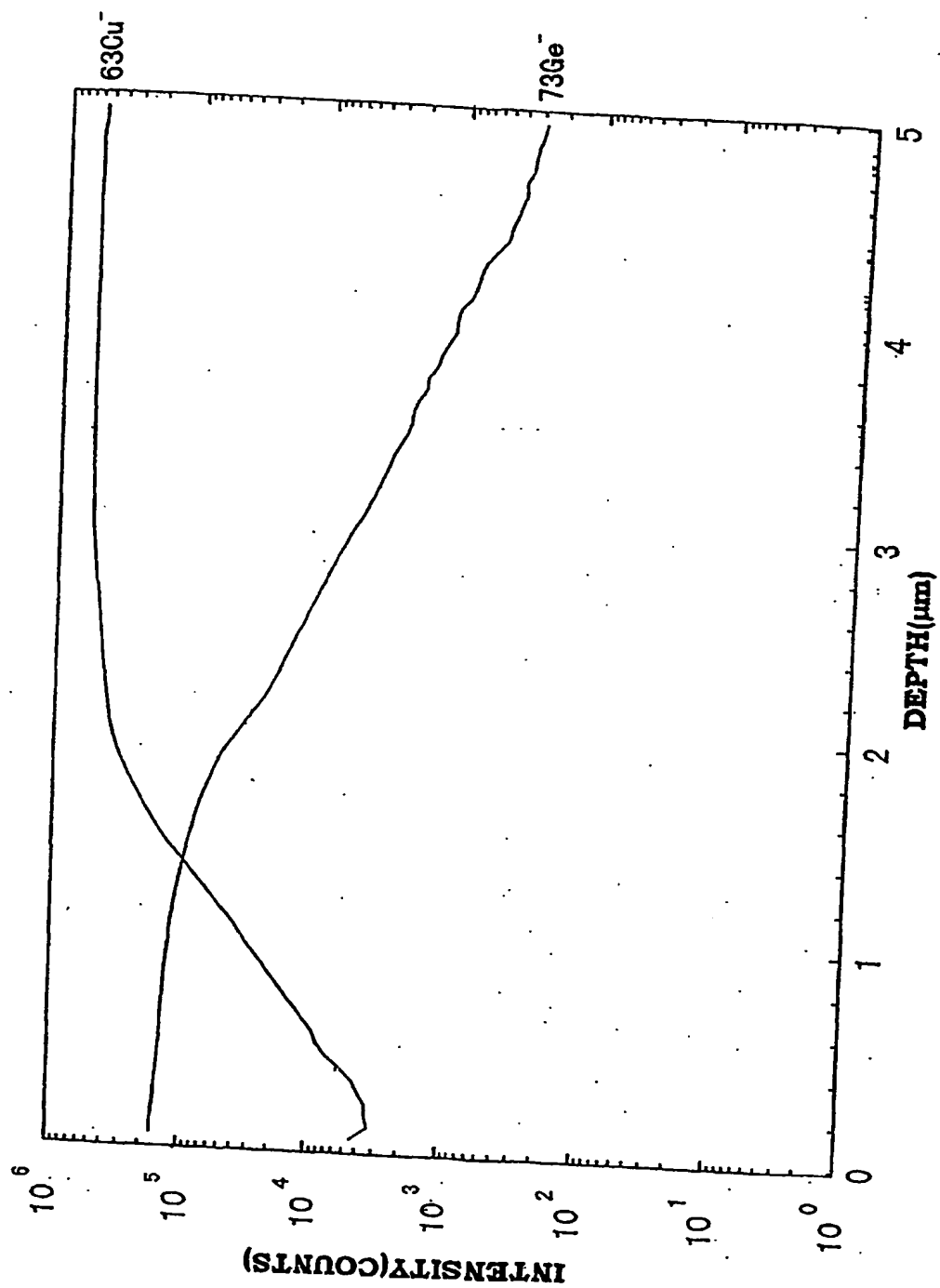


FIG. 38

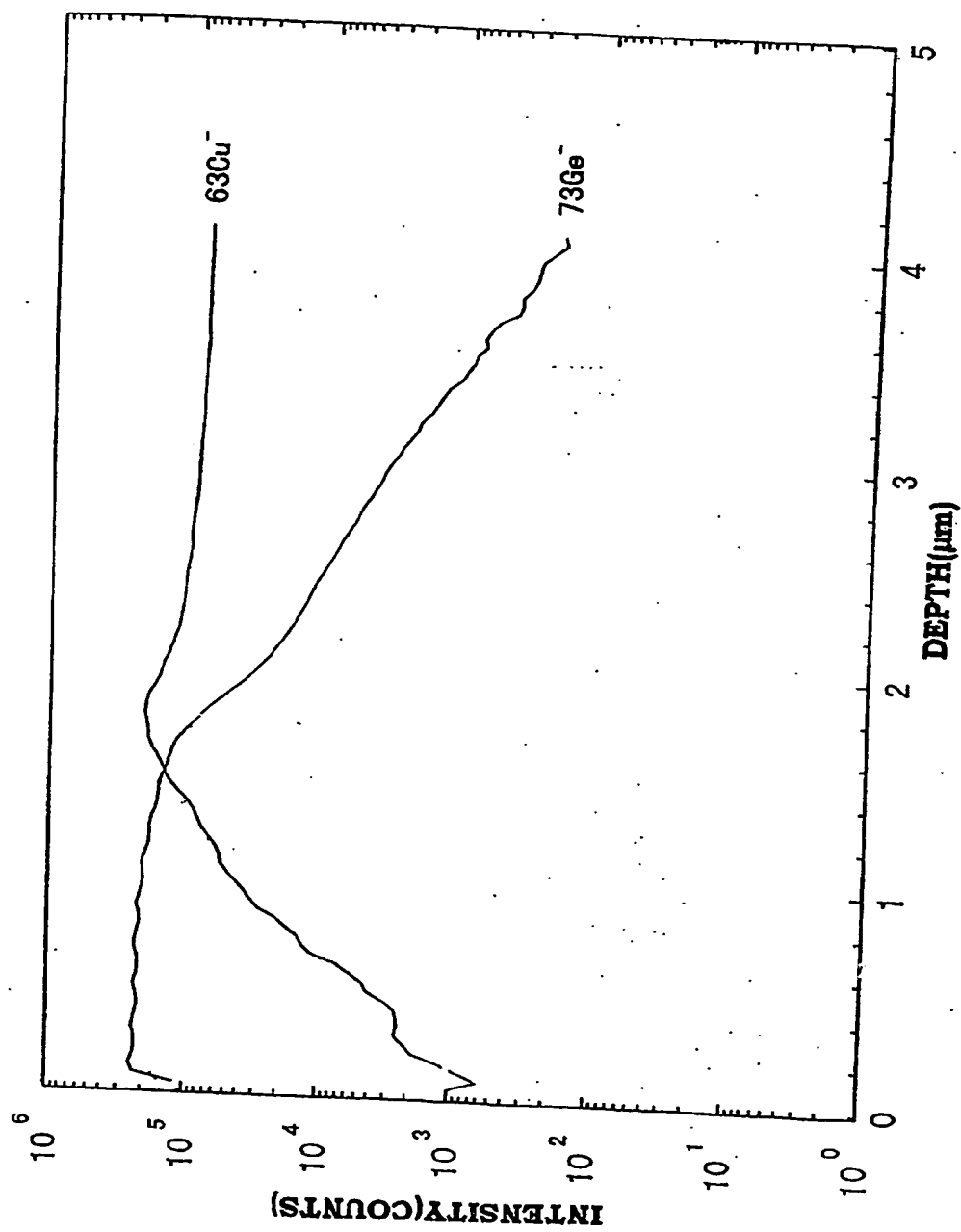


FIG. 39

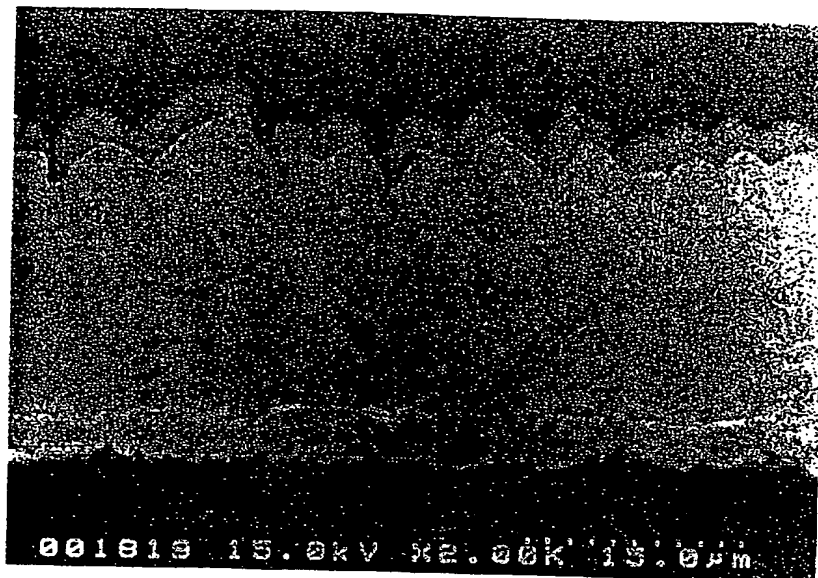


FIG. 40

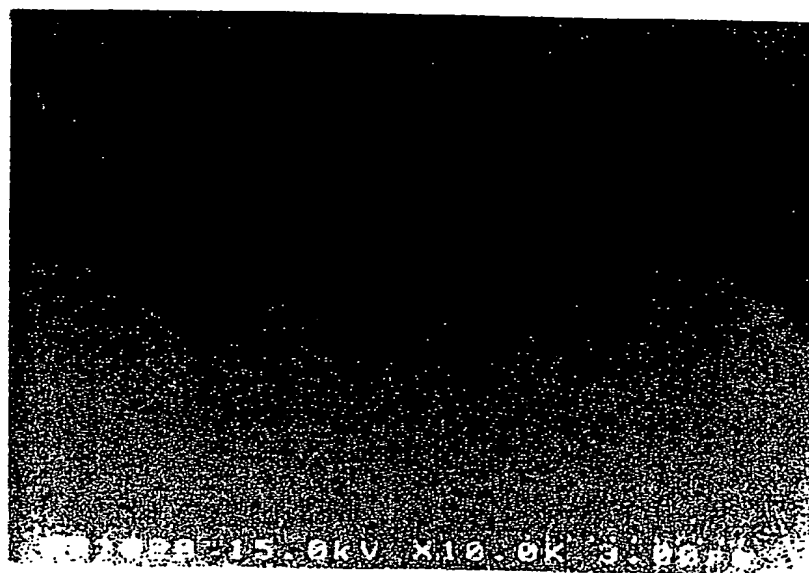


FIG. 41

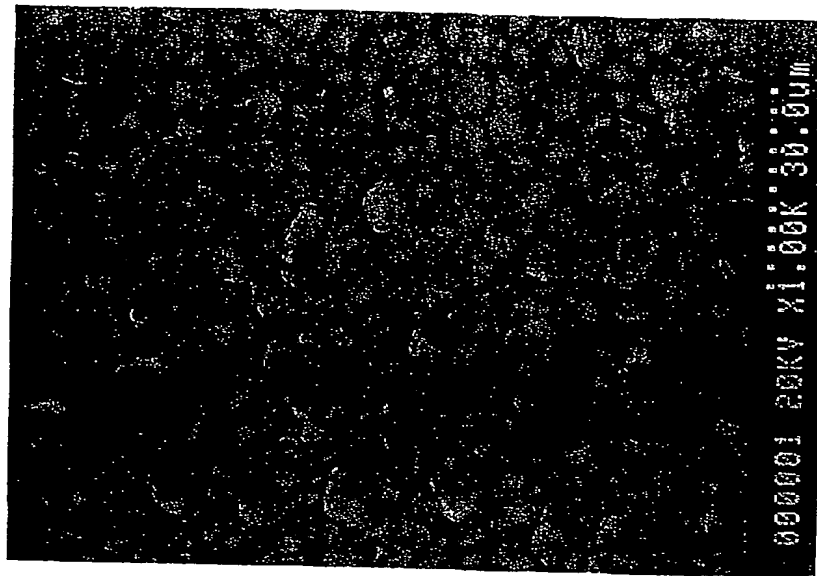


FIG. 42



FIG. 43

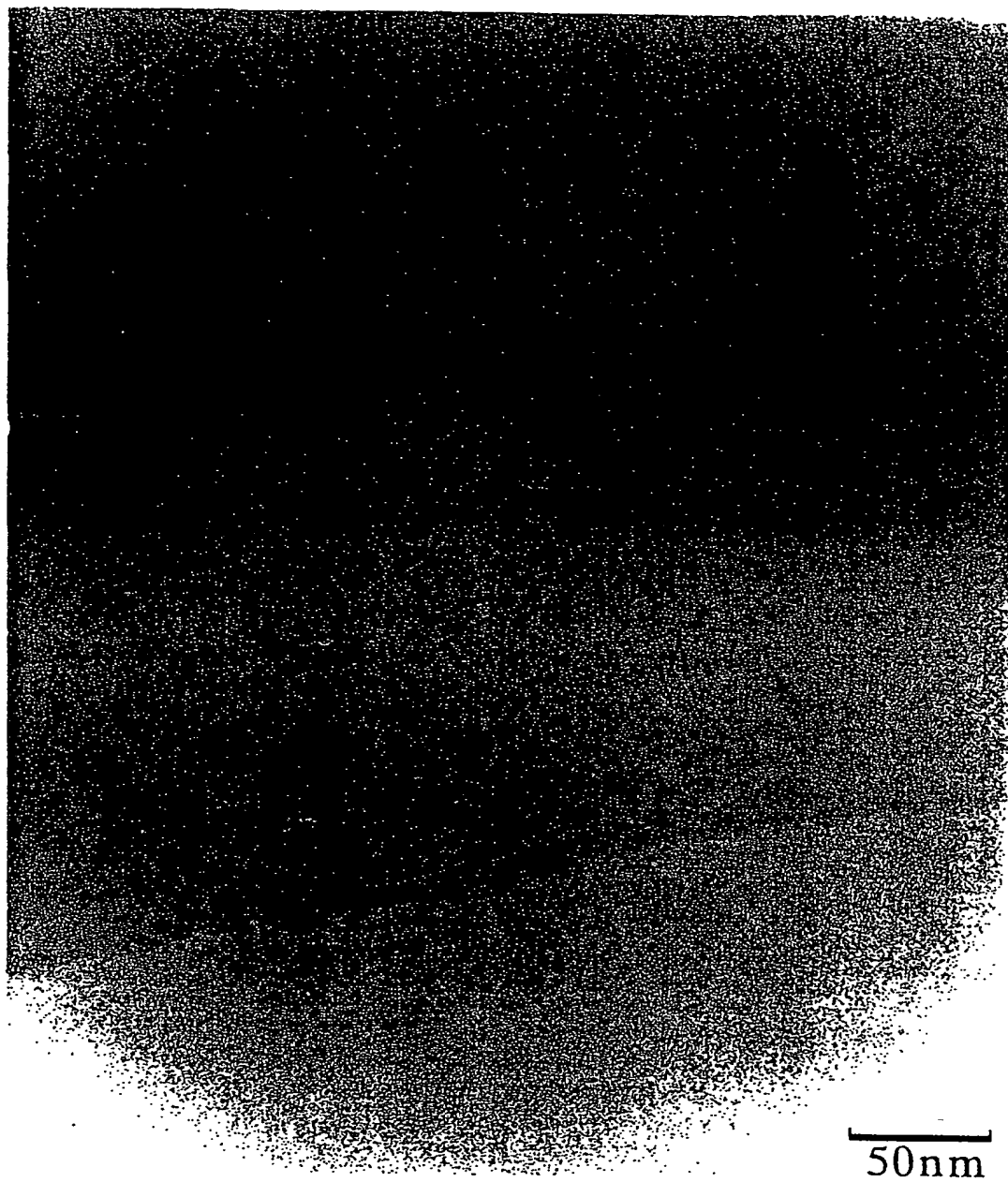


FIG. 44

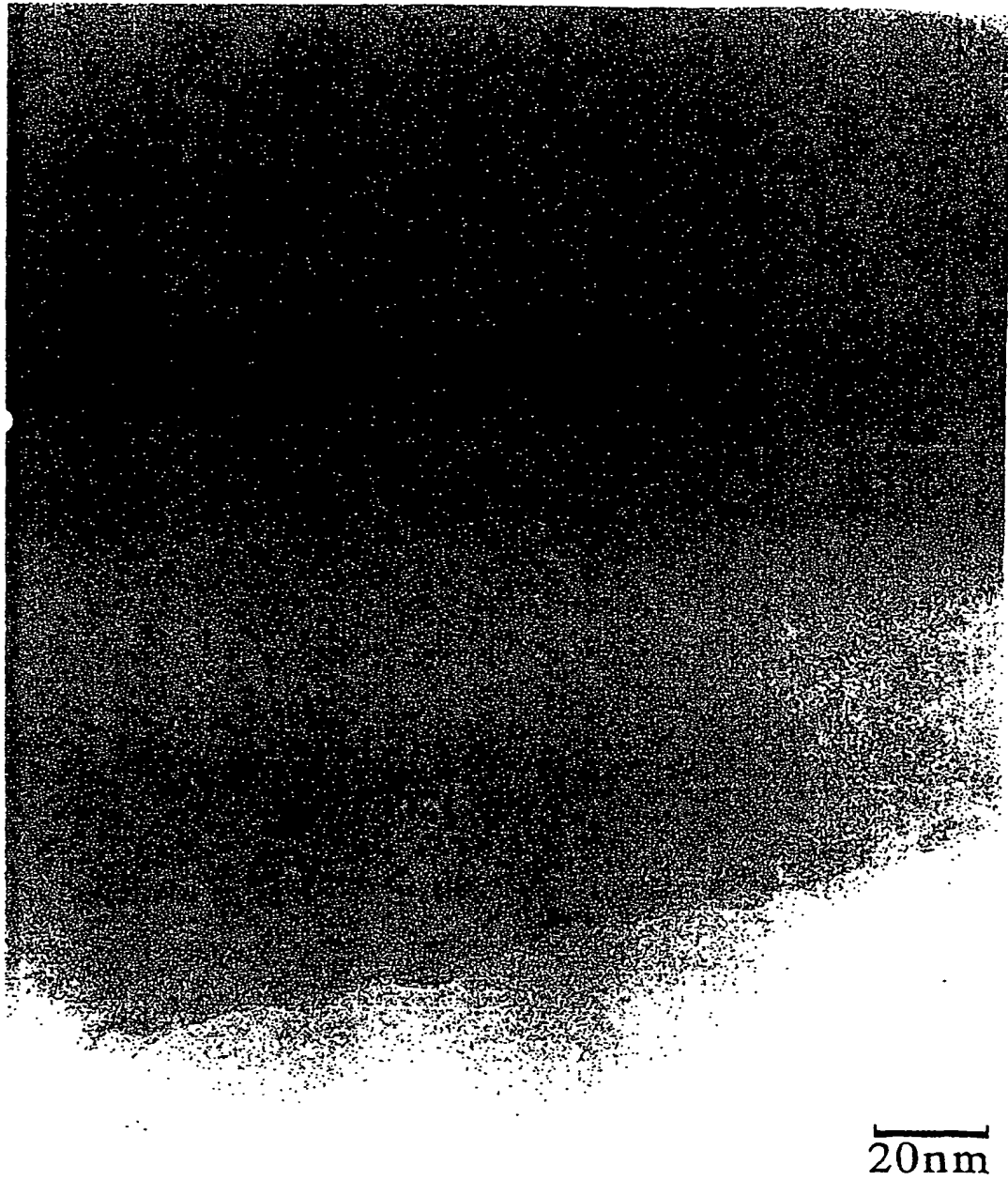


FIG. 45

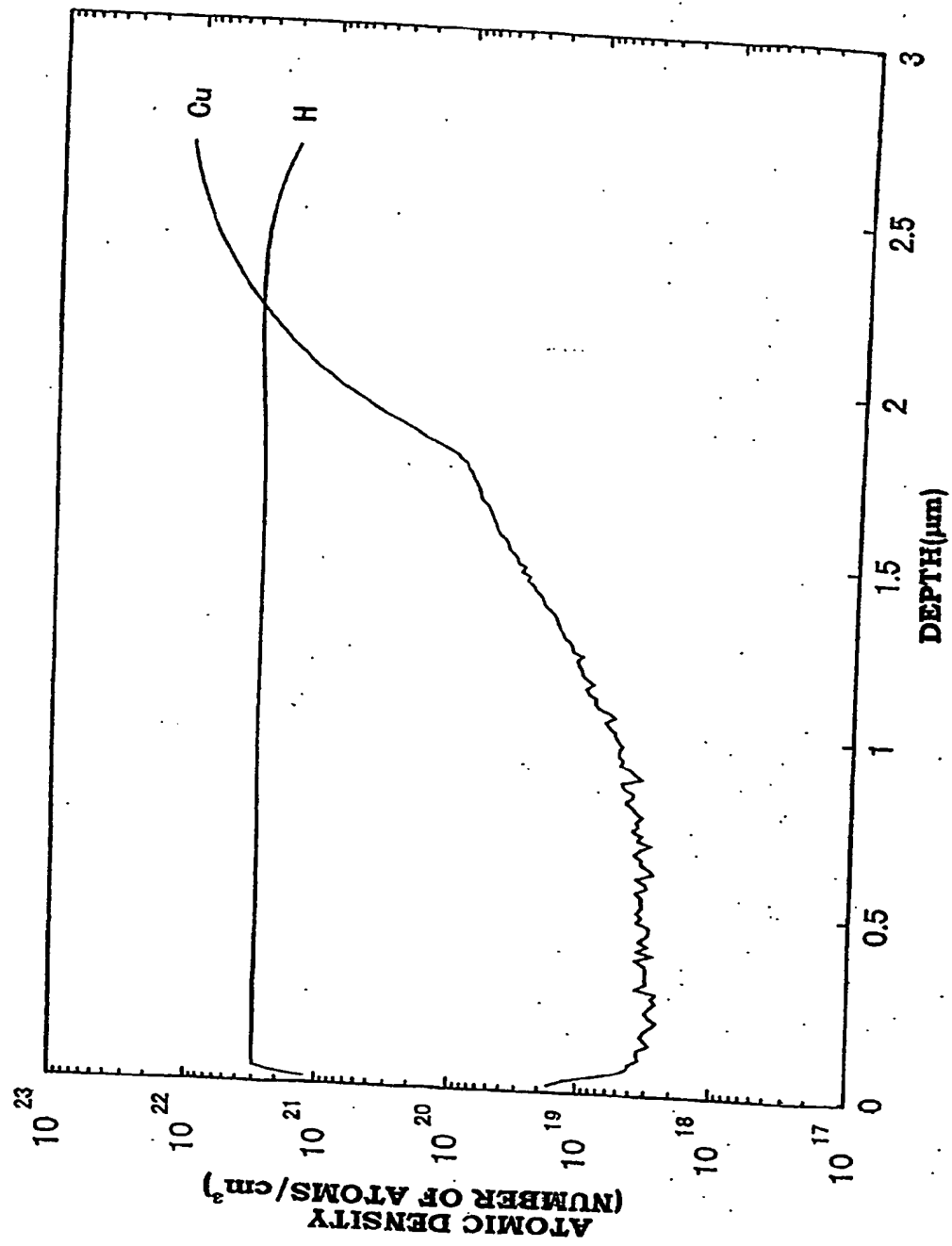
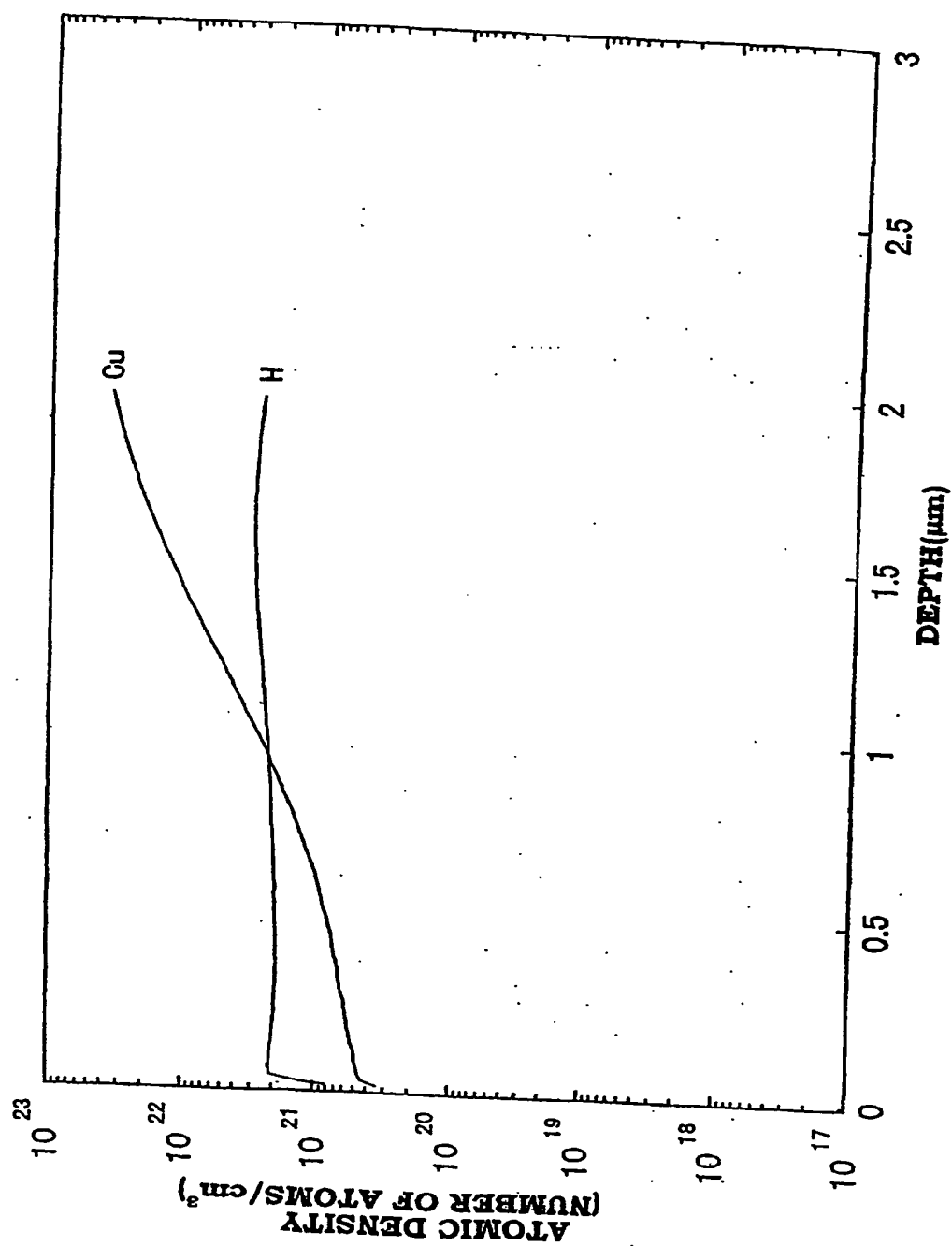


FIG. 46





## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/07292

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int.Cl. <sup>7</sup> . H01M 4/02, 4/04, 4/38, 4/48, 4/58, 4/66, 10/40		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) Int.Cl. <sup>7</sup> . H01M 4/02, 4/04, 4/38, 4/48, 4/58, 4/66, 10/40		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Sinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2000 Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Toroku Koho 1996-2000		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
EX	JP, 2000-208136, A (NEC Corporation), 28 July, 2000 (28.07.00), Claim 1; Par. Nos. 0002, 0003, 0012, 0016, etc. (Family: none)	1, 2, 10, 14, 22, 2 4-26, 31-33, 36, 39, 40, 53-58
X	JP, 11-233116, A (Canon Inc.), 27 August, 1999 (27.08.99),	1-22, 24-40, 44-51, 53-58
Y	Claims 1 to 41; Par. Nos. 0012 to 0027, 0033, 0038, 0042, 0043, 0056 to 0061, example, etc. (Family: none)	23, 41-43, 52
X	JP, 11-154508, A (Toshiba Corporation), 08 June, 1999 (08.06.99),	1, 2, 10-12, 22 24-26, 30-36, 39, 53-58
Y	Claims 1 to 4; Par. Nos. 0023 to 0028; drawings, etc. (Family: none)	3-9, 13-21, 23 27-29, 37, 38, 40-52
X	JP, 10-294098, A (YUASA CORPORATION), 04 November, 1998 (04.11.98),	1, 2, 10-12, 22 24-26, 30-36, 39, 53-58
Y	Claims 1 to 5; Par. No. 0010; example, etc. (Family: none)	3-9, 13-21, 23 27-29, 37, 38,
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 12 December, 2000 (12.12.00)		Date of mailing of the international search report 26 December, 2000 (26.12.00)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/07292

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
		40-52
X	EP, 910131, A (NGK INSULATORS, LTD.), 21 April, 1999 (21.04.99), Claims 1-5; Par. Nos. [0010], [0019]	1,2,10-12,22 24-26,30-36, 39,53-58
Y	(& JP, 11-120990, A Claims 1 to 5; Par. Nos. 0009, 0015, etc. & CA, 2249935, A)	3-9,13-21,23 27-29,37,38, 40-52
Y	EP, 855752, A (CANON KABUSHIKI KAISHA), 29 July, 1998 (29.07.98), Claims 1-135; page 7, lines 20-34; page 8, lines 13-28; page 10, line 49 to page 11, line 3, section of "FORMATION OF ELECTRODE MATERIAL LAYER" (& JP, 11-242954, A Claims 1 to 135; Par. Nos. 0030 to 0036, 0058 to 0115, etc. & CA, 2228095, A & CN, 1194472, A & KR, 98070935, A)	11-22,40,46-51
Y	JP, 11-283628, A (Fuji Photo Film Co., Ltd.), 15 October, 1999 (15.10.99), Par. Nos. 0009 to 0018, 0037 to 0038, etc. (Family: none)	11-22,40,46-51
Y	JP, 9-213339, A (Fuji Photo Film Co., Ltd.), 15 August, 1997 (15.08.97), Claims 1 to 7; Par. Nos. 0009, 0015 to 0037, etc. (Family: none)	11,12,15,16, 23,41-43,52
Y	JP, 11-135130, A (Mitsubishi Aluminum Co., Ltd.), 21 May, 1999 (21.05.99), Claims 1 to 3, 5, 6; Par. Nos. 0003 to 0007, 0021 to 0026, etc. (Family: none)	11,12,23, 41-43,51
Y	JP, 5-74479, A (Asahi Chemical Industry Co., Ltd.), 26 March, 1993 (26.03.93), Claim 1; Par. Nos. 0007 to 0020; example, etc. (Family: none)	11,12,23, 41-43,52
Y	JP, 60-175375, A (Hitachi Maxell, Ltd.), 09 September, 1985 (09.09.85), Claims 1, 2; [Hatsumei no Gaiyou] etc. (Family: none)	28,29,37,38
A	JP, 10-326628, A (Mitsubishi Electric Corporation), 08 December, 1998 (08.12.98) Claims 1 to 10; Figs etc. (Family: none)	1-58
A	US, 5888670, A (Soichiro Kawakami, et al), 30 May, 1999 (30.05.99), Claims 1-60, column 10, lines 13-27 and Figs.1,2 (& JP, 8-321306, A Claims 1 to 61; Par. Nos. 0048, 0049; Figs. 1, 2, etc.)	1-58

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